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CHEMICAL THERMODYNAMICS IN NONFERROUS METALLURGY

(Khimicheskaya termodinamika v tsvetnoi metallurgii)

Vol. III

THERMODYNAMICS OF TUNGSTEN, MOLYBDENUM, TITANIUM, ZIRCONIUM, NIOBIUM, AND TANTALUM AND OF THEIR MORE IMPORTANT COMPOUNDS

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EXPLANATORY LIST OF ABBREVIATIONS OF U.S.S.R. INSTITUTIONS AND JOURNALS APPEARING IN THIS TEXT

Abbreviation	Full name (transliterated)	Translation
AN SSSR	Akademiya Nauk SSSR	Academy of Sciences of the USSR
AN UkrSSR	Akademiya Nauk Ukrainskoi SSR	Academy of Sciences of the Ukrainian SSR
DAN SSSR	Doklady Akademii Nauk SSSR	Transactions of the Academy of Sciences of the USSR
Izv.	Izvestiya	Bulletin
LGU	Leningradskii Gosudarstvennyi Universitet	Leningrad State University
MGU	Moskovskii Gosudarstvennyi Universitet	Moscow State University
SO AN SSSR	Sibirskoe Otdelenie Akademii Nauk SSSR	Siberian Department of the Academy of Sciences of the USSR
ZhFKh	Zhurnal Fizicheskoi Khimii	Journal of Physical Chemistry
ZhNKh	Zhurnal Neorganicheskoi Khimii	Journal of Inorganic Chemistry
ZhOKh	Zhurnal Obshchei Khimii	Journal of General Chemistry
ZhPKh	Zhurnal Prikladnoi Khimii	Journal of Applied Chemistry

PREFACE

In the period between the publication of the second and third volumes of the present work, the XXII Congress of the Communist Party of the Soviet Union adopted a new program containing directives for developing and advancing the production of light, nonferrous and rare metals.

The publication of this reference book, which deals with both production technology and properties of these metals, should be of assistance in this task.

The third volume of the present manual contains data on the thermodynamic properties of tungsten, molybdenum, titanium, zirconium, niobium, and tantalum.

The chapters on tungsten, molybdenum, titanium, and zirconium were prepared by A.L. Lomov, and those on niobium and tantalum by V.I. Lavrent'ev.

Critical comments on the book and suggestions concerning its contents or presentation of the data should be sent to the publishing house. They will be taken into consideration in subsequent editions of this manual.

Chapter 1

THERMODYNAMIC PROPERTIES OF TUNGSTEN AND OF ITS MORE IMPORTANT COMPOUNDS

1. METALLIC TUNGSTEN (M = 183.92)

Crystal structure, density, melting point

Isotopes of tungsten. According to Aston /1/, and Landolt-Börnstein /2/, five isotopes of tungsten occur in nature.

Mass number	180	182	183	184	186
Content in %	0.16	26.35	14.32	30.68	28.49

Atomic volume of tungsten. The atomic volume of tungsten as determined by various authors is given in Table 1.

TABLE 1

Atomic volume of tungsten

Atomic volume	Method of determination	Year	Author	Reference
9.57	X-ray	1926	Barth	/3/
9.53	X-ray	1928	Becker	/4/
9.59	Calculated for atomic weight 184.0 and density 19.2	1930	Biltz	/5/

Allotropy of tungsten. Tungsten exists in two allotropic modifications, α and β. The β-modification is formed by the reduction of WO_3 with dry hydrogen at temperatures below 630°. The transition point α-W → β-W is at approximately 630°.

Crystal structure of tungsten. α-Tungsten has a cubic crystal structure of type A2. Space group O_h^9, a = 3.1589 Å (Neuburger /6/, Petch /7/, Rooksby /8/, and Moeller /9/). β-Tungsten exhibits a cubic crystal structure of type A 15, a = 5.04 Å, space group O_h^3. For the structure of β-tungsten see /11 and 12/.

Density of tungsten. The density of vacuum melted tungsten is 19.0 — 19.2 g/cm^3, according to Wartenberg /13/, and 18.72 g/cm^3, according to Weiss /14/. Fink /15/ found that tungsten powder, when pressed and subsequently sintered in an electric furnace, exhibited a density of 18.81 g/cm^3. Wire produced from such tungsten had densities of 19.3, 19.58 to 19.64, and 19.86 g/cm^3 at a diameter of 3.75, 0.25, and 0.38 mm, respectively. The

density of monocrystal tungsten is 19.9 to 19.3 /17/ or 19.35 g/cm^3 /18/. The X-ray density of tungsten is 19.37 /16/, 19.32 ± 0.02 /19/, 19.32 /4/, 19.295 /20/, and 19.363 g/cm^3 /21/. Sebesta determined the density of tungsten pycnometrically and found it to be 19.35 g/cm^3 /21/.

The densities of tungsten as determined by earlier studies show large discrepancies. These are dependent on the amount of oxide and carbide impurities and also on the porosity of the metal sample. Porosity has a considerable influence as shown by the investigations of Geiss and Liempt /18/. These workers studied tungsten rods, made by sintering at 1300° and subsequently forged (from diameter 3.75 mm) and drawn. These workers calculated the following density values for the respective diameters (Table 2).

TABLE 2

Density of tungsten

Diameter, mm	Density, g/cm^3	Diameter, mm	Density, g/cm^3
Forged		Drawn	
14.8	17.62	0.15	19.23
11.8	18.28	0.11	19.22
6.2	19.16	0.02	19.41 ± 0.04
5.0	19.19	0.0125	19.28 ± 0.05
3.85	19.22		

Thermal expansion of tungsten. The coefficient of thermal expansion of tungsten is 4.4×10^{-6} between 20 and 630°, 5.1×10^{-6} between 630 and 1340°, and 6.2×10^{-6} between 1340 and 2150°.

Melting point of tungsten. This value can be determined by optical methods only. Table 3 contains data on the melting point and radiation constants C_2 obtained by various authors.

TABLE 3

Melting point of tungsten /23/

C_2	Melting point, °C	Year	Author
14,600	3200 3080	1960	Waidner, Burgess
14,600	2900	1910	Wartenberg
14,500	2974 3027	1911	Forsythe
14,200	3100 ± 60	1912	Pirani, Meyer
14,800	3267 ± 30	1916	Langmuir
14,600	3357	1916	Worthing

Worthing /24/ compared his data with the data of the authors shown in Table 3, with the exception of those of Waidner and Burgess, and calculated the melting point of tungsten for the radiation constants C_2 14350 and 14300. The results of these calculations are shown in Table 4.

TABLE 4

Melting point of tungsten, °C

Radiation constant C_2		Author
14,350	14,300	
3348	3362	Wartenberg
3521	3538	Pirani, Meyer
3593	3611	Forsythe
3614 ± 30	3636 ± 30	Langmuir
3667 ± 20	3690 ± 20	Worthing

Luckey /25/ found the following values of melting points for tungsten in a nitrogen atmosphere under various pressures. He melted tungsten electrodes in an electric arc.

Pressure, atm	1	8	14	21
Melting point, °C	3350	3321	3309	3289

Table 5 contains values of the melting point of tungsten given as reliable by various reference books.

TABLE 5

Melting point of tungsten

Melting point, °C	Year	Author	Reference
3387	1936	Kelley	/26/
3380	1956	Kubaschewski, Evans	/27/
3370	1949	Stull	/28/
3377	1956	Stull and Sinke	/29/
3380	1952	Rossini et al.	/51/
(3655°K) 3382°C	1952	Smithells	/52/

We, ourselves, consider the correct melting point of tungsten to be that proposed by Stull and Sinke /29/, i.e., 3377°.

Vapor pressure and boiling point of tungsten

Boiling point of tungsten. The boiling point of tungsten computed from vapor pressure curves is given in Table 6.

TABLE 6

Boiling point of tungsten

Boiling point, °K	Year	Author	Reference
5110	1913	Langmuir	/30/
5105	1920	Liempt	/31/
5222	1925	Zwikker	/32/
6970	1927	Jones, Langmuir, Mackay	/33/

Kubaschewski and Evans /27/ consider the boiling point of tungsten to be approximately 5400°K. According to the data of Kelley /34/ and of Stull and Sinke /29/ the boiling point of tungsten is 6203° and 5800°K, respectively.

Vapor pressure of tungsten. The vapor pressures of tungsten are given in Table 7 (Zwikker /32/).

TABLE 7

Vapor pressure of tungsten /32/

Temperature, °K	Vapor pressure P, mm Hg	Temperature, °K	Vapor pressure P, mm Hg
1927	$100 \cdot 10^{-15}$	2642	$430 \cdot 10^{-9}$
2093	$9.5 \cdot 10^{-12}$	2831	$8.3 \cdot 10^{-6}$
2220	$246 \cdot 10^{-12}$	3049	$130 \cdot 10^{-6}$
2331	$2 \cdot 10^{-9}$	3287	$1.74 \cdot 10^{-3}$
2504	$51 \cdot 10^{-9}$	3426	$6.5 \cdot 10^{-3}$

Langmuir /35/ found the following values for the vapor pressures of tungsten.

Temperature, °K	2500	2700	2900	3100
Vapor pressure P, mm Hg	$2.94 \cdot 10^{-7}$	$6.95 \cdot 10^{-6}$	$1.06 \cdot 10^{-4}$	$1.14 \cdot 10^{-3}$

The vapor pressure was calculated from the rate of evaporation in vacuo, which was determined by the loss in weight of an incandescent tungsten wire.

Langmuir, working with Jones and Mackay /33/, later corrected his own data /35/ and also converted the pressures from mm Hg to bars.

The corrected and converted results are given in Table 8.

TABLE 8

Vapor pressure of Tungsten
(Langmuir, Jones, and Mackay /33, 35/)

Temperature, °K	Vapor pressure P, in bars	Temperature, °K	Vapor pressure P, in bars	Temperature, °K	Vapor pressure P, in bars
1200	$1.88 \cdot 10^{-22}$	3000	$9.09 \cdot 10^{-2}$	5000	$1.2 \cdot 10^{4}$
1500	$2.86 \cdot 10^{-15}$	3300	1.55	5400	$3.9 \cdot 10^{4}$
1700	$2.89 \cdot 10^{-12}$	3500	7.55	5600	$6.8 \cdot 10^{4}$
2000	$1.32 \cdot 10^{-8}$	3655	23.3	6000	$1.7 \cdot 10^{5}$
2300	$6.32 \cdot 10^{-6}$	3800	58	6400	$3.8 \cdot 10^{5}$
2500	$1.71 \cdot 10^{-4}$	4200	$51 \cdot 10^{2}$	6800	$8.8 \cdot 10^{5}$
2700	$2.77 \cdot 10^{-3}$	4600	$2.9 \cdot 10^{3}$	6970	$1.0 \cdot 10^{6}$

Langmuir derived the following equation for the vapor pressure of tungsten:

$$\log P \text{ (mm Hg)} = 15.502 - \frac{47444}{T} - 0.9 \log T.$$

Liempt /31/ modified Langmuir's equation as follows:

$$\log P\,(\text{atm}) = -\frac{46440}{T} + 9.15.$$

The vapor pressures of liquid tungsten from 3820 to 5920°K, as calculated by Kelley /34/, are:

Temperature, °K	3820	4210	4710	5350	5660	5920	6200
Vapor pressure, atm	0.0001	0.001	0.01	0.1	0.25	0.5	1.00

Vapor pressures of liquid tungsten, as given by Stull /28/, are:

Temperature, °C	3990	4337	4507	4690	4886	5007	5168	5403	5666	5927
Vapor pressure, mm Hg	1	5	10	20	40	60	100	200	400	760

Kubaschewski and Evans /27/ suggested the following equation for the variation of the vapor pressure of tungsten with temperature, valid from 2000 to 3500°.

$$\log P\,(\text{mm Hg}) = -\frac{42000}{T} - 0.146 \log T - 0.164 \cdot 10^{-3} T + 9.84.$$

The data of Stull /29/ are the most reliable, since they were compiled by this author from numerous data obtained by other workers. We recommend the Kubaschewski-Evans equation /27/ for the calculation of the vapor pressure of solid tungsten.

Heat capacity. Heat capacity change during evaporation and sublimation. Heat, entropies, and free energies of fusion, boiling, and sublimation.

Heat capacity of tungsten. The average specific heat capacity of tungsten is given in Table 9.

TABLE 9

Average specific heat capacity of tungsten

Temperature range, °C	Average specific heat capacity cal/deg·g	Year	Author	Reference
-185 to + 20	0.0357	1907	Nordmeyer, Bernoulli	/36/
-252 to −196	0.0095	1913	Dewar	/37/
0 — 20	0.0320	1932	Jaeger, Rosenbohm	/38/
15 — 93	0.0340	1901	Defacqz, Guichard	/39/
19 — 100	0.0358	1910	Weiss, Stimmelmayr	/40/
15 — 258	0.0366	1901	Defacqz, Guichard	/39/
15 — 423	0.0375			
2095 — 2212	0.0479	1922	Smith, Bigler	/41/
2102 — 2202	0.045	1925	Bockstahler	/42/

Table 10 shows the calculated values of average specific heat capacity of solid tungsten from 19.7 to 500.3°K. These calculations are based on the results obtained by Bronson, Chisholm, and Dockerty /43/, who measured

the heat capacity of tungsten calorimetrically at 28°. The calculated data are in very good agreement with experimental results.

TABLE 10

Mean specific heat capacity of tungsten

Temperature °K	Average specific heat capacity cal/deg·g	Temperature °K	Average specific heat capacity cal/deg·g	Temperature °K	Average specific heat capacity cal/deg·g
19.7	0.03120	133.5	0.03209	287.8	0.03263
30.2	0.03136	140.6	0.03212	288.8	0.03264
54.5	0.03171	142.7	0.03213	312.3	0.03270
64.8	0.03176	145.9	0.03214	317.5	0.03272
66.2	0.03177	151.5	0.03216	336.4	0.03277
66.3	0.03177	164.9	0.03221	372.3	0.03287
68.9	0.03179	183.4	0.03229	417.2	0.03299
71.1	0.03180	185.6	0.03230	420.3	0.03300
75.6	0.03182	200.3	0.03235	421.1	0.03300
76.3	0.03182	206.4	0.03237	422.0	0.03301
92.1	0.03190	216.5	0.03241	444.4	0.03305
98.1	0.03193	238.8	0.03248	469.0	0.03312
110.4	0.03199	286.7	0.03263	500.3	0.03319

TABLE 11

True specific heat capacity of tungsten

Temperature °C	Temperature °K	True specific heat capacity cal/deg·g	Year	Author	Reference
340	—	0.033	1912	Pirani	/44/
1000	—	0.036	1912		
1350	—	0.041	1912		
-247.1	—	0.00116	1924	Lange	/45/
-234.3	—	0.00408	1924		
-218.4	—	0.0098	1924		
-182.0	—	0.0198	1924		
0	—	0.0368	1926	Magnus, Danz	/46/
450	—	0.0394	1926		
900	—	0.0420	1926		
100	—	0.03215	1928	Geiss, Liempt	/47/
—	100	0.0205	1928	Zwikker	/48/
—	200	0.0288	1928		
—	300	0.0321	1928		
—	600	0.0339	1928		
—	900	0.0357	1928		
0	—	0.03199	1930	Jaeger, Rosenbohm	/49/
100	—	0.03247	1930		
300	—	0.03343	1930		
500	—	0.03438	1930		
700	—	0.03533	1930		
900	—	0.03626	1930		
1100	—	0.03718	1930		
1300	—	0.03809	1930		
1500	—	0.03900	1930		
1600	—	0.03935	1930		

Data on the true specific heat capacities of tungsten as calculated by various authors are given in Table 11.

The average and true atomic heat capacities of tungsten are presented in Table 12 and Table 13, respectively.

TABLE 12

Average atomic heat capacity of tungsten

Temperature, °C	Average atomic heat capacity, cal/g·atom deg	Year	Author	Reference
-253 to -196	1.75	1913	Dewar	/37/
-185 to + 20	6.57	1907	Nordmeyer, Bernouilli	/36/
15 — 93	6.26	1901	Defaeqz, Guichard	/39/
14 —423	6.90	1901	Defaeqz, Guichard	/39/
2095—2212	8.75	1922	Smith, Bilger	/41/
2102—2202	8.3	1925	Bockstahler	/42/
0—20	5.89	1930	Jaeger, Rosenbohm	/49/

TABLE 13

True atomic heat capacity of tungsten

Temperature		True atomic heat capacity cal/g·atom deg		Year	Author	Reference
°C	°K	C_p	C_v			
-247.1	—	0.21	—	1924	Lange	/45/
-234.3	—	0.75	—	1924		
-218.4	—	1.8	—	1924		
-182.0	—	3.6	—	1924		
0	—	6.78	—	1926	Magnus, Danz	/46/
450	—	7.25	—	1926		
900	—	7.72	—	1926		
340	—	6.1	—	1912	Pirani	/44/
1000	—	6.6	—	1912		
1350	—	7.5	—	1912		
100	—	5.915	—	1928	Geiss, Liempt	/47/
—	100	3.77	3.77	1928	Zwikker	/48/
—	200	5.32	5.30			
—	300	5.90	5.87			
—	600	6.23	6.15			
—	900	6.57	6.44			
100	—	5.885	—	1930	Jaeger, Rosenbohm	/49/
300	—	6.150	—			
500	—	6.325	—			
700	—	6.500	—			
900	—	6.670	—			
1100	—	6.840	—			
1300	—	7.010	—			
1500	—	7.175	—			
1600	—	7.240	—			

Kelley /50/ proposed the following heat capacity values for solid tungsten at low temperatures.

Temperature, °K	10	25	50	100	150	200	298.1
Atomic heat capacity, C_p cal/g·at. deg	(0.02)	0.21	1.47	3.90	5.00	5.51	5.97

Table 14 contains atomic heat capacities of solid tungsten and of gaseous tungsten as an ideal monatomic gas from 288 to 3000°K (Stull and Sinke /29/).

TABLE 14

Atomic heat capacities of solid and gaseous tungsten /29/

Temperature, °K	Atomic heat capacity C_p cal/g·at. deg		Temperature, °K	Atomic heat capacity C_p cal/g·at. deg		Temperature, °K	Atomic heat capacity C_p cal/g·at. deg	
	solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten
298	5.92	5.09	1200	6.67	9.79	2200	7.49	7.50
300	5.92	5.10	1300	6.75	9.57	2300	7.58	7.38
400	6.00	5.54	1400	6.83	9.30	2400	7.66	7.29
500	6.09	6.30	1500	6.91	9.01	2500	7.74	7.23
600	6.17	7.25	1600	7.00	8.72	2600	7.82	7.18
700	6.25	8.22	1700	7.08	8.45	2700	7.91	7.15
800	6.34	9.03	1800	7.16	8.21	2800	7.99	7.13
900	6.42	9.58	1900	7.24	7.99	2900	8.07	7.14
1000	6.50	9.86	2000	7.33	7.80	3000	8.15	7.15
1100	6.58	9.90	2100	7.41	7.63			

According to Rossini et al. /51/, the molar heat capacities of solid and liquid tungsten are 5.97 and 5.0903 cal/mole · deg., respectively. These values are very close to the molar heat capacity values of Stull and Sinke /29/ and of Kelley /50/.

Influence of temperature on heat capacity of tungsten. The following equations were derived for the specific and atomic heat capacities from 100 to 900° by Magnus and Holzmann /53/.

$$c_p = 0.032036 + 0.045292 \cdot 10^{-4}t,$$

$$C_p = 5.8547 + 8.338 \cdot 10^{-4}t.$$

Jaeger and Rosenbohm /49/ propose the following equations for the specific and atomic heat capacities of tungsten for temperatures of 0°C and above.

$$c_p = 0.03199 + 0.04848 \cdot 10^{-4}t - 0.1174 \cdot 10^{-9}t^2,$$

$$C_p = 5.8861 + 8.9204 \cdot 10^{-4}t - 2.16 \cdot 10^{-8}t^2.$$

Kelley /54/ recommends using the following equation for the calculation of molar heat capacities from 298 to 2000°K:

$$C_p = 5.74 + 0.76 \cdot 10^{-3}T.$$

We recommend the use of this equation in calculations, since it yields more accurate results than the equations of Magnus and Holzmann /53/ and of Jaeger and Rosenbohm /49/.

Heat of fusion of tungsten. The data of Liempt /31/, Jones, Langmuir, and Mackay /33/ on the heat of fusion of tungsten, which were obtained experimentally, show great differences, viz., L_{fus} = 1000 to 5000 cal/g·atom /31/ and L_{fus} = 11,200 cal/g·atom /33/.

Data on the heats of fusion of tungsten obtained by Kelley /55/ (8420 cal/g·atom) and by Kubaschewski and Evans /27/ (8400 cal/g·atom), on the other hand, show very good agreement; Stull and Sinke /29/ propose the same values as Kelley /55/. We consider the heat of fusion of tungsten as proposed by Stull and Sinke /29/ (8420 cal/g·atom) as the most reliable.

Entropy of fusion of tungsten. At T_{melt} = 3660°K, ΔS_{fus} = 2.3 cal/g·atom·deg.

Heat capacity change of tungsten during vaporization. The heat capacity change of tungsten during vaporization is ΔC_P = 4.0 cal/g·atom·deg. /34/.

Heat of vaporization of tungsten. Table 15 shows the heat of vaporization of tungsten as determined experimentally by various authors.

TABLE 15

Heat of vaporization of tungsten

Temperature, °C	Heat of vaporization, cal/g·atom	Year	Author	Reference
-273	217800	1913	Langmuir	/30/
-273	221000	1925	Zwikker	/32/
-273	191800	1927	Jones, Langmuir Mackay	/33/
room	223900	1914	Wintemitz	/56/
boiling point	211500	1920	Liempt	/31/
2400	190000	1925	Becker	/57/

Table 16 shows the most reliable values for the heat of vaporization of tungsten, either at room temperature or at the boiling point.

TABLE 16

Reliable values for the heats of vaporization of tungsten

Temperature, °C	Heat of vaporization, cal/g·atom	Year	Author	Reference
25	199638	1935	Kelley	/34/
5929	176018			
5400	183000	1956	Kubaschewski, Evans	/27/
—	191000	1956	Stull, Sinke	/28/

Langmuir /30/ derived the following equation for the variation of the heat of vaporization with temperature:

$$L_{vap}(\text{cal/g·atom}) = 217800 - 1.8T.$$

According to Kelley /34/, this variation is expressed by the following equation:

$$L_{vap}\,(\text{cal/g}\cdot\text{atom}) = 200830 - 4.0T.$$

Entropy of vaporization of tungsten /34/. At the boiling point T_{boil} = 6203°K the entropy of vaporization is given by ΔS_{vap} = 28.4 cal/g·atom · deg.

Free energy* of vaporization of tungsten. The free energy of vaporization of tungsten is given by ΔF^0_{298} = 187,563 cal/g·atom. This value was calculated from the following equation:

$$\Delta F^0_T = 200{,}830 + 9.2\,T \log T - 67.27\,T \text{ /34/.}$$

Rossini et al. /51/ proposed ΔF^0_{298} = 191,600 cal/g · atom.

Heat capacity change of tungsten during sublimation. Since $C_P = 5.65 + 0.866 \times 10^{-3}T$ for solid tungsten and C_P = 4.97 for liquid tungsten, Kelley /34/ derived the following equation for the change of heat capacity of tungsten as a function of temperature:

$$\Delta C_p = -0.68 - 0.866 \cdot 10^{-3}T \text{ cal/g} \cdot \text{atom} \cdot \text{deg.}$$

Heat of sublimation of tungsten. The heat of sublimation of tungsten, calculated from the expression:

$$L_{subl} = \Delta H^0_T = 202{,}900 - 0.68T - 0.433 \cdot 10^{-3}T^2,$$

is given by $L_{subl} = \Delta H^0_T$ = 202,659 cal/g · atom (Kelley /34/). According to Rossini et al. /51/, $L_{subl} = \Delta H^0_{298}$ = 201.6 kcal/g · atom. According to Stull and Sinke /29/, the heat of sublimation of tungsten varies from 298 to 3000°K, as shown in Table 17.

TABLE 17

Heat of sublimation of tungsten

T, °K	L_{subl} cal/g· atom	T, °K	L_{subl} cal/g· atom	T, °K	L_{subl} cal/g· atom
298	200000	1200	201644	2200	203095
300	199999	1300	201942	2300	203088
400	199932	1400	202206	2400	203062
500	199917	1500	202441	2500	203018
600	199980	1600	202628	2600	202958
700	200133	1700	202786	2700	202894
800	200367	1800	202909	2800	202808
900	200605	1900	202998	2900	202721
1000	200989	2000	203057	3000	202626
1100	201328	2100	203089		

Free energy of sublimation of tungsten. The free energy of sublimation of tungsten ΔF^0_{298} = 191,507 cal/g · atom.

Kelley gives the following equation for the determination of this value /34/:

$$\Delta F^0_T = 202{,}900 + 1.57T \log T + 0.433 \cdot 10^{-3}T^2 - 42.23T \text{ cal/g} \cdot \text{atom.}$$

Rossini et al. /51/ give the following value: ΔF^0_{298} = 191.6 kcal/g · atom.

* [Referred to in the Russian original as "Isobaric potential", represented by the symbol "Z".]

Table 18 gives log P and the free energy of sublimation of solid tungsten from 298 to 3000°K /29/.

TABLE 18

Free energy of sublimation and log P for solid tungsten

Temperature, °K	ΔF_{subl} cal/g·atom	− log P	Temperature, °K	ΔF_{subl} cal/g·atom	− log P	Temperature, °K	ΔF_{subl} cal/g·atom	− log P
298	190009	139.286	1200	159368	29.027	2200	123433	12.261
300	189949	138.389	1300	155831	26.199	2300	119828	11.386
400	186608	101.966	1400	152268	23.772	2400	116206	10.581
500	183282	80.118	1500	148711	21.668	2500	112568	9.840
600	179946	65.550	1600	145124	19.822	2600	108968	9.159
700	176599	55.141	1700	141518	18.193	2700	105370	8.528
800	173215	47.324	1800	137911	16.743	2800	101728	7.939
900	169813	41.239	1900	134313	15.448	2900	98147	7.396
1000	166359	36.361	2000	130677	14.279	3000	94536	6.886
1100	162594	32.367	2100	127048	13.221			

Enthalpy, entropy, and free energy function of tungsten

Enthalpy of tungsten. Lange /45/ reports the enthalpy values of tungsten in joules. We converted his values to calories, using the conversion factor 4.1840 J = 1 cal at 15°C. The resulting data, converted to calories for temperatures below room temperature, are as follows:

Temperature, °K	50	100	150	200	250	273.1	298.1
Enthalpy, cal/g·atom*	20	161	388	652	937	1073	1224

The enthalpies of solid tungsten at temperatures exceeding room temperature are given in Table 19 /54/.

TABLE 19

Enthalpies of tungsten according to Kelley /54/

T, °K	$H_T^0 - H_{298}^0$ cal/g·atom	T, °K	$H_T^0 - H_{298}^0$ cal/g·atom	T, °K	$H_T^0 - H_{298}^0$ cal/g·atom
400	615	1000	4360	1600	8430
500	1220	1100	5010	1700	9130
600	1830	1200	5670	1800	9840
700	2450	1300	6340	1900	10550
800	3080	1400	7030	2000	11260
900	3710	1500	7730		

* According to Lange /45/, one bar denotes an accuracy of up to ±0.7 cal/g·atom, whereas two bars denote a higher accuracy.

The enthalpies of solid tungsten from 288 to 2000°K are calculated according to the following equation:

$$H_T^0 - H_{298}^0 = 5.74T + 0.38 \cdot 10^{-3}T^2 - 1745 \text{ cal/g} \cdot \text{atom}.$$

The accuracy of this equation is within 0.5%.

Table 20 contains enthalpies of solid and gaseous tungsten (considered as ideal monoatomic gas) in the temperature range 298° to 3000°K. For solid tungsten $H_{298}^0 - H_0^0 = 1486$ cal/g · atom /29/.

TABLE 20

Enthalpies of solid and gaseous tungsten according to Stull and Sinke/29/

T, °K	Enthalpy $H_T^0 - H_{298}^0$ cal/g·atom		T, °K	Enthalpy $H_T^0 - H_{298}^0$ cal/g·atom	
	solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten
298	0	0	1700	9110	11896
300	10	9	1800	9820	12729
400	606	538	1900	10540	13538
500	1211	1128	2000	11270	14327
600	1824	1804	2100	12010	15099
700	2445	2578	2200	12760	15855
800	3075	3442	2300	13510	16598
900	3710	4375	2400	14270	17332
1000	4360	5349	2500	15040	18058
1100	5010	6338	2600	15820	18778
1200	5680	7324	2700	16600	19494
1300	6350	8292	2800	17400	20208
1400	7030	9236	2900	18200	20921
1500	7710	10151	3000	19010	21636
1600	8410	11038			

Entropy of tungsten. According to Lange /45/, the entropies of tungsten in the solid state at low temperatures are as follows:

Temperature, °K	50	100	150	200	250	273.1	298.1
Entropy, cal/g·atom*	0.58	2.41	4.23	5.76	7.07	7.58	8.10

The entropies of solid and gaseous tungsten as experimentally determined by various authors are given in Table 21.

Table 22 contains the entropy values of solid and gaseous tungsten, as given in various reference books.

The entropies of tungsten at high temperatures are shown in Table 23 /54/.

Stull and Sinke /29/ give the entropy values of tungsten quoted in Table 24.

Free energy function. Stull and Sinke /29/ term the expression $-\frac{F_T^0 - H_{298}^0}{T}$, which is a function of the free energy reduced potential.

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* See footnote on previous page.

TABLE 21

Entropies of solid and gaseous tungsten

Entropy S°_{298} cal/g·atom deg	Year	Author	Reference
	Solid tungsten		
8.4	1917	Lewis, Gibson	/58/
16.6	1928	Herz	/59/
8.2	1958	Desorbo	/61/
	Gaseous tungsten		
40.7	1920	Tolman	/62/

TABLE 22

Entropies of solid and gaseous tungsten

Entropy S°_{298} cal/g·atom deg	Year	Author	Reference
	Solid tungsten		
8.4	1931	Mellor	/60/
8.1	1924	Lange	/45/
8.04± 0.1	1950	Kelley	/50/
8.0	1952	Rossini et al.	/51/
8.0± 0.2	1956	Kubaschewski, Evans	/27/
	Gaseous tungsten		
41.56± 0.01	1950	Kelley	/50/
41.552	1952	Rossini et al	/51/

TABLE 23

Entropies of tungsten

Temperature, °K	$S^{\circ}_T - S^{\circ}_{298}$ cal/mole deg	Temperature, °K	$S^{\circ}_T - S^{\circ}_{298}$ cal/mole deg
400	1.77	1300	9.19
500	3.12	1400	9.70
600	4.23	1500	10.18
700	5.19	1600	10.63
800	6.03	1700	11.06
900	6.77	1800	11.47
1000	7.46	1900	11.85
1100	8.08	2000	12.21
1200	8.65		

It is more commonly referred to as "the free energy function". These values are given for tungsten in Table 25. The free energy function values in the second column refer to solid tungsten, those in the third column to ideal monoatomic gaseous tungsten.

TABLE 24

Entropy of solid and gaseous tungsten, cal/g · atom deg

T, °K	S°_T		T, °K	S°_T		T, °K	S°_T	
	solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten
298	8.04	41.55	1200	16.68	51.91	2200	20.95	57.16
300	8.08	41.58	1300	17.22	52.69	2300	21.29	57.49
400	9.79	43.10	1400	17.72	53.39	2400	21.61	57.80
500	11.14	44.41	1500	18.20	54.02	2500	21.92	58.10
600	12.25	45.64	1600	18.65	54.59	2600	22.23	58.38
700	13.21	46.83	1700	19.07	55.11	2700	22.53	58.65
800	14.05	47.99	1800	19.48	55.59	2800	22.81	58.91
900	14.80	49.08	1900	19.87	56.02	2900	23.10	59.16
1000	15.48	50.11	2000	20.24	56.43	3000	23.37	59.40
1100	16.11	51.05	2100	20.60	56.81			

TABLE 25

Free energy function

T, °K	$-\frac{F^\circ_T - H^\circ_{298}}{T}$		T, °K	$-\frac{F^\circ_T - H^\circ_{298}}{T}$		T, °K	$-\frac{F^\circ_T - H^\circ_{298}}{T}$	
	solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten		solid tungsten	gaseous tungsten
298	8.04	41.55	1200	11.95	45.81	2200	15.15	49.26
300	8.05	41.55	1300	12.34	46.32	2300	15.42	50.28
400	8.28	41.76	1400	12.70	46.80	2400	15.67	50.58
500	8.72	42.16	1500	13.06	47.26	2500	15.91	50.88
600	9.21	42.64	1600	13.40	47.70	2600	16.15	51.16
700	9.72	43.16	1700	13.72	48.12	2700	16.39	51.43
800	10.21	43.69	1800	14.03	48.52	2800	16.60	51.70
900	10.68	44.23	1900	14.31	48.91	2900	16.83	51.95
1000	11.12	44.77	2000	14.61	49.27	3000	17.04	52.19
1100	11.56	45.29	2100	14.89	49.62			

2. OXIDES OF TUNGSTEN

At present, the following oxides of tungsten are known: WO_2, WO_3, intermediate oxides $WO_{2.72}$ ($W_{18}O_{49}$) or $13\,WO_3 \cdot 5\,WO_2$ and $WO_{2.9}$($W_{20}O_{58}$) or $18\,WO_3 \cdot 2\,WO_2$.

These data of Vasil'eva, Gerasimov, and Simanov /63/ are in good agreement with those of Glemser and Sauer /64/, who found the following compounds in the W—O system.

$WO_3 - WO_{2.95}$, α phase,
$WO_{2.92} - WO_{2.88}$, β phase,
$WO_{2.76} - WO_{2.65}$, γ phase,
$WO_{2.03} - WO_2$, δ phase.

The dimensions of the monoclinic cell of $WO_{2.72}$ are $a = 18.24 \pm 0.02$ kX; $b = 3.767 \pm 0.05$ kX; $c = 13.95 \pm 0.02$ kX; $\beta = 115.14° \pm 0.07$.

The unit cell of $WO_{2.90}$ is monoclinic and its lattice parameters are: $a = 12.03 \pm 0.01$ kX; $b = 3.759 \pm 0.005$ kX; $c = 23.54 \pm 0.02$ kX; $\beta = 94.72° \pm 0.05$ /85/ and /147/. The crystal structure of $WO_{2.90}$ is identical with that of ReO.

This paragraph deals with physical and thermodynamic properties of the oxides WO_2 and WO_3 only. Some of the thermodynamic parameters of the intermediate oxides of tungsten will be found on pp. 42 and 44.

Tungsten dioxide WO_2 (M = 215.92)

Crystal structure of WO_2. The monoclinic tungsten dioxide has a distorted rutile structure. Kubaschewski and Evans /27/ recommend the following constants for the monoclinic lattice of WO_2: $a = 5.65$ Å, $b = 4.89$ Å, $c = 5.55$ Å, and $\alpha = 120°25'$.

Density of WO_2. The density of this compound, according to Gmelin /65/, is 11.4 g/cm^3.

Molar volume of WO_2. The molar volume of this compound is 18 cm^3/mole /66/.

Hardness of WO_2. The hardness of WO_2 is 5.0—5.5 on the Mohs hardness scale (Friedrich and Sittig) /67/.

Melting point of WO_2. The melting point of WO_2 is between 1500 and 1600°K, according to Friedrich and Sittig /67/.

Boiling point of WO_2. According to Alterthum and Koreff /68/, the boiling point of WO_2 is about 2000°K.

Sublimation temperature of WO_2. The sublimation temperature of tungsten dioxide was investigated by Wöhler and Balz /69/. These authors showed that sublimation of this compound begins at 800°.

Later studies by Meerson /70/ showed that at 1050° considerable sublimation of WO_2 takes place.

Brewer reports /71/ that tungsten dioxide disproportionates at 2125 ± 50°K, and 1 atm according to the equation:

$$3WO_2\,(s) \rightarrow W\,(s) + 2WO_3\,(g).$$

Heat capacity of WO_2. Gerasimov et al. /63/ derived the following equation for the heat capacity of WO_2:

$$C_p = 17.83 + 1.89 \cdot 10^{-3}T - 3.342 \cdot 10^{5}T^{-2}$$

The authors used this equation for calculation of the standard thermodynamic data of WO_2. The accuracy of this equation is ±3%. It was derived by using the value of $C_{P_{298}}$ for WO_2, according to Venturini /72/, the values for C_P for solid bodies at their transition temperatures, and the average equations for the oxides UO_2 /73/, VO_2 /27/, and ThO_2 /27/, whose values of $C_{P_{298}}$ are close to that of WO_2.

Heat of sublimation of WO_2. The heat of sublimation of this compound was calculated by Blackburn et al. /74/, who measured the vapor pressure over WO_2 by the Knudsen effusion method. It was found that WO_2 disproportionates into gaseous WO_3 and solid tungsten with the liberation of heat $L_{subl} = \Delta H^{\circ}_{1500} = -90.2$ kcal/mole (WO_2).

Entropy of WO_2. The absolute entropy of WO_2, according to Griffis /75/, is $S^0_{298} = 17.1 \pm 1.0$ e.u. Gerasimov et al. /76/ calculated the entropy $S^0_{298} = 15.0 \pm 1.5$ e.u. for WO_2, using the entropies of tungsten (S^0_{298}), according to Clusius and Zosine /77/, and of O_2, according to Kelley /78/. Griffis /79/ gives the value $S^0_{298} = 19.7 \pm 1$ e.u. Kubaschewski and Evans /27/ consider the value $S^0_{298} = 15 \pm 2.5$ e.u. to be the most reliable for WO_2. This absolute entropy value for WO_2 and also the value $S^0_{298} = 15.0 \pm 1.5$ e.u. should be used in thermodynamic calculations.

Heat of formation of WO_2. The experimentally determined heats of formation of WO_2(s) are given in Table 26. It can be seen from this table that the results, particularly those obtained in the last few years, are in good agreement.

TABLE 26

Heat of formation of WO_2 (s)

Heat of formation $-\Delta H^{\circ}_{298}$ kcal/mole	Method	Year	Author	Reference
122.8	Calculated from data of dissociation pressures	1922	Liempt	/80/
138.0	Calculated from reduction reactions [redox reactions]	1929	Shibata	/81/
135.0 ± 0.3	Calculated for data on heterogeneous equilibria studied from 500 to 1000° by a static method	1958	Griffis	/75/
137.0 ± 1.0	Calorimetrically	1958	Griffis	/79/
134.8 ± 0.1	"	1959	Morozova, Getskina	/82/
140.94 ± 0.2	—	1952	Mah	/83/
136.6 ± 2	Emf.	1960	Gerasimov et al.	/76/

Table 27 contains the most reliable values of heats of formation of WO_2.

TABLE 27

Most reliable values for heats of formation of WO_2

Heat of formation $-\Delta H^{\circ}_{298}$ kcal/mole	Year	Author	Reference
134.2	1953	Brewer	/71/
136.0	1952	Rossini et al.	/51/
134.0 ± 2.5	1956	Kubaschewski, Evans	/27/

Alterthum and Koreff /68/ calculated the heat of formation of gaseous WO_2 for the reaction $W(s) + O_2 = WO_2(g)$. This calculation, taking into account also the heat of vaporization of WO_2, gives 82.6 kcal/mole as the result.

Entropy of formation of WO_2. Brewer /71/ considers the value $\Delta S^0_{298} = -41.0$ cal/mole · degrees as the most reliable for the entropy of formation of $WO_2(s)$.

Gerasimov and co-workers /76/ calculated the entropy of formation of solid WO_2 from emf data. Their value, $\Delta S^0_{298} = -41.7 \pm 1.5$ e.u., is in good agreement with that of Brewer /71/.

Free energy of formation of WO_2. Brewer /71/ considers the value $\Delta F^0_{298} = -122$ kcal/mole for the free energy of formation of solid WO_2 as the most reliable. The corresponding value of Gerasimov et al. /76/, obtained by emf measurements ($\Delta F^0_{298} = -124.0 \pm 2$ kcal/mole), is very close to that of Brewer /71/.

Kubaschewski and Evans give /27/ the following temperature variation for the free energy for the equation $W(s) + O_2(g) = WO_2(s)$

$$\Delta F_T = -131{,}600 + 36.6T \text{ cal/mole.}$$

This expression permits calculation of ΔF_T values with an accuracy of ±5 kcal in the temperature range 298 to 1500°K.

Tungsten trioxide WO_3 ($M = 231.92$)

Allotropy of WO_3. Ueda and Ichinokawa /84/ found three modifications of WO_3 stable in the following temperature ranges: α-WO_3, room temperature to 720°, β-WO_3 720 to 1100°, and γ-WO_3, at temperatures above 1100°.

Crystal structure of WO_3. Vasil'eva, Gerasimov, and Simanov /63/ studied the crystalline structure of WO_3 by X-ray methods. They found that the lattice of α-WO_3 is identical with the monoclinic lattice described by Magnelli and co-workers /85/. Magnelli found the following lattice parameters: $a = 6.270_2 \pm 0.003kX$, $b = 7.501_7 \pm 0.003kX$, $c = 3.827 \pm 0.002kX$, $\beta = 90.90°$. Vasil'eva, Gerasimov, and Simanov /63/ found the following values for the lattice parameters from X-ray powder diagrams of β-WO_3: $a = 7.29_3kX$, $b = 7.48_0kX$, $c = 3.83_8kX$, $\alpha = \beta = \gamma = 90°$.

Density of WO_3. According to Smith and Exner /88/ the density of WO_3 is 7.157 g/cm^3.

Molar volume of WO_3. Biltz /110/ found that the molar volume of WO_3 is 32.3 cm^3/mole.

Temperature of transition of WO_3. According to Ueda and Ichinokawa /84/, $\alpha \rightleftharpoons \beta$- and $\beta \rightleftharpoons \gamma$-transitions take place at 720 and 1100°, respectively.

Melting point of WO_3. The melting point of WO_3, according to Jaeger and Germs /89/, is approximately 1473°. During the solidification a supercooling of 80° is observed. Kubaschewski and Evans /27/, and Brewer /71/, consider the above-mentioned temperature the most reliable, whereas Rossini and co-workers /51/ recommend the value $t_{melt} = 1470°$.

Boiling point of WO_3. According to Kubaschewski and Evans /27/, the boiling point of WO_3 is approximately 1850°. Brewer /71/ considers the value 2100 ± 100°K as the most reliable.

Temperature of sublimation of WO_3. The temperature of the beginning of sublimation was determined by Wöhler and Baltz /69/. According to these authors, this temperature is between 800 and 900°. The temperature of the beginning of sublimation was more accurately determined by Meerson /70/, i.e., 850°. Jaeger and Germs /89/ showed that at 1200° 35% of WO_3 sublimes within ten minutes. According to Rossini /51/, the sublimation temperature of WO_3 is 1102° at a pressure of 0.0058 mm Hg.

Vapor pressure of WO_3.

Temperature, °K	933	1026	1175	1253	1353	1460	1508	1630*	2000**
Vapor pressure, mm Hg	0.0193	0.206	3.23	9.09	41.1	144.0	294.0	760	760

The temperature variation of the vapor pressure of WO_3 from 1000°K to the melting point is expressed by the following equation /27/:

$$\log P\,(\text{mm Hg}) = -\frac{24{,}600}{T} + 15.63.$$

Heat capacity of WO_3. The heat capacity of WO_3 between 135°K and approximately 320°K was studied by Russel /91/. This author gives the following values for the average specific heat capacities:

Temperature, °K	83.9 to 191.6	197.2 to 273	275 to 319.6
Average specific heat capacities, cal/g · deg	0.0442	0.0678	0.0783

The true heat capacities for the corresponding temperatures, according to Russel /91/, are given in Table 28.

TABLE 28

Heat capacity of WO_3, according to Russel /91/

Temperature, °K	True molar heat capacity	
	C_{det}, cal/mole · degree	C_{calc}, cal/mole · degree
138	10.25	10.57
235	15.73	16.39
297	18.16	18.46

The molar heat capacity of crystalline WO_3 at low temperatures has the following values:

Temperature, °K	10	25	50	100	150	200	298.1
Molar Heat Capacity, cal/degree · mole	(0.06)	(0.82)	(3.15)	7.76	11.91	15.11	19.50

The calculation of the molar heat capacity of WO_3 from 298 to 1550°K can be carried out by the following formula given by Kelley /54/:

$$C_P = 17.48 + 6.79 \cdot 10^{-3} T.$$

Kubaschewski and Evans /27/ consider the accuracy of this formula for the above range to be 6%.

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* Extrapolated.

** Calculated by Born /90/.

In their calculations of the thermodynamic parameters of β-WO_3, Gerasimov and co-workers used the following equation /95/:

$$C_p = 16.356 + 10.67 \cdot 10^{-3}T,$$

which was derived by Sawada /92/. This expression may also be used for the calculation of ΔH^0_{298}, ΔF^0_{298}, and ΔS^0_{298} of tungsten trioxide.

Rossini and co-workers /51/ give the value $C_{P_{298}} = 19.48$ cal/mole·degree for the molar heat capacity of tungsten.

Heat of vaporization of WO_3. The heat of vaporization of WO_3 at 1 atm., as given by Born /90/, is 49 kcal/mole. This value, as calculated by Alterthum /17/ according to Trouton's rule, is 40.64 kcal/mole.

Heat of sublimation of WO_3. The heat of sublimation of WO_3 is approximately 122.0 and 109.0 kcal/mole at 25° and at the melting point (1473°) /5/, respectively. According to Vyeno /93/, $L_{subl} = 112.6$ kcal/mole at 1368.1°K.

Rossini /51/ gives the following value for the heat of sublimation of WO_3: $L_{subl} = 112$ kcal/mole at 1102° and 0.0058 mm Hg.

Entropy of sublimation of WO_3. The entropy of sublimation of WO_3 is $\Delta S_{subl} = 81$ cal/deg·mole at 1102° and 0.0058 mm Hg. According to Vyeno /93/, $\Delta S_{subl} = 58.4$ cal/degree·mole at 1368.1°K.

Free energy of sublimation of WO_3. According to Vyeno /93/, the free energy of sublimation of WO_3 is $\Delta F^0_{298} = 95.2$ kcal/mole. At 1368.1°K, $\Delta F_{subl} = 32.7$ kcal/mole.

Energy of dissociation of WO_3. The energy of dissociation of gaseous WO_3 into atoms at 0°K is $D_0 = 465 \pm 7$ kcal/mole /71/.

Entropy of WO_3. Vasil'eva, Gerasimov, and Simanov /94/, /95/ calculated the values for the standard entropies of α- and β-WO_3 to be $S^0_{298} = 20.0$ e.u. and $S^0_{298} = 17.6$ e.u., respectively. These data are in good agreement with the values found by other authors. Thus, Seltz et al. /103/ determined the standard entropy at 25°C as $S^0_{298} = 19.9$ e.u. Rossini and coworkers /51/ and also Kubaschewski and Evans /27/ obtained the same value for the standard entropy of WO_3. The latter authors consider the value 19.9 e.u. to be accurate within ± 0.2 e.u.

Heat of formation of WO_3. Table 29 gives experimental data of various authors for the heat of formation of WO_3 from simple compounds.

Table 30 gives the most reliable values for the heat of formation of WO_3 from simple compounds.

In the opinion of Gerasimov and Vasil'eva /102/ the most reliable value for the heat of formation of WO_3 is $\Delta H^0_{298} = -200.2$ kcal/mole.

We recommend this value for thermodynamic calculations.

The heat of formation of WO_3 from simpler compounds is given with a fair degree of accuracy by the following equation:

$$\Delta H^0_T = -194{,}800 - 0.73T + 3.24 \times 10^{-3}T^2 - 2.816 \times 10^5 T^{-1} \text{ cal/mole.}$$

The data of Seltz /103/ fit well into this equation.

Entropy of formation of WO_3. The experimental values of the entropy of formation are given in Table 31.

Brewer considers the value −61.5 kcal/mole·deg. as the most reliable for the entropy of formation of WO_3.

In the authors' opinion, the value $\Delta S^0_{298} = -61.65$ e.u. as the most reliable.

TABLE 29

Heat of formation of WO_3

Heat of formation, ΔH°_{298} kcal/mole	Method	Year	Author	Reference
195.8	–	1908	Mixter	/96/
193.5	At constant pressure and room temperature in bomb	1910	Weiss et al.	/14/
196.7	From the reaction [W]+[Na_2O_2] and [WO_3]+[Na_2O] at constant pressure	1910	Mixter	/97/
192.7	–	1910	Weiss et al.	/14/
195 ± 1	–	1923	Van Liempt	/98/
195.7	In bomb	1924	Moose, Parr	/99/
199.9	Calculated from the equilibrium constant of reduction by carbon monoxide	1929	Shibata	/81/
193.825	–	1942	de Kay-Thompson	/100/
195.67	–	1943	Seltz et al.	/103/
200.2	At constant pressure	1948	Huff et al.	/101/
205.3	Equilibrium of tungsten oxides and hydrogen; WO_3 (β)	1957	Gerasimov et al.	/95/
193 ± 1	Heterogeneous equilibrium $H_2 - W - WO_2 - H_2O$ for $WO_{2.90}$	1958	Griffis	/75/
203.0	Equilibrium of tungsten oxides with hydrogen WO_3 (α)	1960	Vasil'eva, Gerasimov and Simanov	/94/

TABLE 30

Recommended values of heats of formation of WO_3

Heat of formation ΔH°_{298}, kcal/mole	Year	Author	Reference
200.84	1952	Rossini et al.	/51/
200.1 ± 0.3	1953	Brewer	/71/
200.0 ± 0.5	1956	Kubaschewski, Evans	/27/

Free energy of formation of WO_3. Table 32 shows the experimental data of various authors on the free energy of formation of WO_3 from the elements.

According to Brewer /71/ the free energy of formation of WO_3 is −181.6 kcal/mole. Rossini /51/ considers the most reliable value to be −182.47 kcal/mole.

Temperature variation of the free energy of formation of WO_3. Seltz and co-workers /103/ give the following equation for the temperature variation of the free energy:

$$\Delta F^{\circ}_{T} = -194{,}800 + 0.73T \ln T - 3.24\times10^{-3}T^2 - 1.408\times10^{5}T^{-1} + 57.10T \text{ cal/mole.}$$

TABLE 31

Entropy of formation of WO_3

Entropy of formation $-\Delta S^{\circ}_{298}$ e.u.	Year	Author	Reference
61.65	1924	Moose, Parr	/99/
52.8	1942	de Kay-Thompson	/100/
68.4	1948	Huff et al.	/101/
61.65	1943	Seltz et al.	/103/
61.6*	1960	Vasil'eva, Gerasimov and Simanov	/94/
63.9**	1957	Vasil'eva, Gerasimov and Simanov	/95/

* α-WO_3.
** β-WO_3.

TABLE 32

Free energy of formation of WO_3

Free energy of formation $-\Delta F^{\circ}_{298}$ kcal/mole	Year	Author	Reference
177.3	1924	Moose, Parr	/99/
226.16	1938	Abichandari, Jatkar	/104/
177.3	1943	Seltz et al.	/103/
178.079	1942	de Kay-Thompson	/100/
182.47	1947	Huff et al.	/101/
186.2*	1957	Vasil'eva, Gerasimov, Simanov	/95/
184.7**	1960	Vasil'eva, Gerasimov, Simanov	/94/

* β-WO_3.
** α-WO_3.

Kubaschewski and Evans /27/ give the following equation for the temperature variation of

$$\Delta F^{0}_{T} = -201.5 - 10.2 \times 10^{-3} T \log T + 0.097 \times T \text{ kcal/mole.}$$

This equation is valid from 298 to 1400°K with an accuracy of ±5 kcal.

3. SULFIDES OF TUNGSTEN

Tungsten disulfide WS_2 (M = 248.052)

Crystal structure of WS_2. Tungsten sulfide has the crystal structure of the MoS_2 type with the following lattice parameters: a = 3.18 Å, b = 12.5 Å /27/.

Temperature of decomposition of WS_2. Picon /105/ heated WS_2 to 1100° in vacuo and did not observe any changes in the composition of this compound. At 1200°, however, approximately a 60% loss in the sulfur content was observed. A complete decomposition of WS_2 was observed at 2000°.

Vapor pressure of WS_2. No data are available.

Heat capacity of WS_2. No data are available.

Entropy of WS_2. Rossini /51/ gives the following values for the absolute entropy of WS_2: $S^0_{298} = 23$ cal/mole · degree. According to Kubaschewski and Evans /27/, the absolute entropy value S^0_{298} for $WS_{1.95-2.00}$ is 22.4 ± 3.0 cal/mole · degree.

Heat of formation of WS_2. Table 33 shows tentative values for the heat of formation of WS_2 from its elements.

TABLE 33

Heat formation of WS_2

Heat of formation $-\Delta H^0_{298}$ kcal/mole	Year	Author	Reference
46.32	1937	Kelley	/107/
46.3	1952	Rossini	/51/
46.4 ± 5.0	1956	Kubaschewski, Evans	/27/

Free energy of formation of WS_2. According to Kelley /107/, the free energy of formation of WS_2 is $\Delta F^0_{298} = -46{,}150$ cal/mole. Rossini gives the value $\Delta F^0_{298} = -46.2$ kcal/mole.

The temperature variation of the free energy of formation of WS_2 according to the reaction W(s) + 2S(rhomb) = WS_2(s) is expressed by the equation

$$\Delta F_T = -45{,}840 + 3.68T \log T - 10.14T \text{ cal/mole (Kelley /77/).}$$

Kubaschewski and Evans /27/ gave the same equation and showed that its accuracy is ±8 cal.

4. HALIDES OF TUNGSTEN

Tungsten hexafluoride WF_6 (M = 297.92)

Crystalline structure of WF_6. No data are available.

Temperature of transition of WF_6. Barber and Cady give this value as −8.2 ± 0.1° /108/. They claim to be the first to have determined this value for WF_6 from its cooling curve.

Melting point of WF_6. The melting point of WF_6 was determined by Ruff and Ascher and found to be 2.3° /138/. Barber and Cady /108/ investigated some physical properties of WF_6 and observed a break on the cooling curve corresponding to the melting point 2.0 ± 0.3°.

The best available values of the melting point of WF_6 are the following: $t_{melt} = -0.5°$ (Kelley /34/, Stull /28/), $t_{melt} = 0.0°$ (Kubaschewski, Evans /27/), t_{melt} (at P = 420 mm Hg) = 2.5° (Rossini /51/).

Boiling point of WF_6. Barber and Cady /108/ determined the boiling point from the pressure-temperature curve for liquid WF_6 to be 17.06 ± 0.05°. This value is somewhat lower than that reported by Ruff and Ascher (17.5°) /138/.

Kelley /34/ gives the boiling point of WF_6 as 290.4°K, Kubaschewski and Evans /27/, as 17°C.

Vapor pressure of WF_6. Values were determined by Barber and Cady /108/ and are given in Table 34.

Table 34

Vapor pressure of WF_6

Temperature, °C	Pressure, mm Hg	Temperature, °C	Pressure, mm Hg
11.83	619.64	34.20	1401.6
15.00	701.68	37.11	1542.7
17.15	762.29	39.65	1674.8
19.46	831.9	41.90	1799.1
22.42	929.7	44.20	1935.3
25.24	1029.2	46.72	2088.9
27.99	1134.1	49.13	2247.8
30.74	1244.9	51.38	2403.5

These values were calculated from the equation

$$\log P\,(\text{mm Hg}) = 6.88699 - \frac{928.580}{T} - \frac{67942.9}{T^2}$$

The vapor pressures of solid and liquid WF_6 were also measured by Ruff and Ascher /138/ and their data are quoted by Kelley /34/

Temperature, °K	182.4	199.4	220.9	248.8	262.3(s)	273.2(l)	290.4
Vapor pressure, atm.....	0.0001	0.001	0.01	0.1	0.25	0.5	1.00

Stull /28/ quotes Ruff and Ascher /138/ and Kelley /34/ and gives values for the vapor pressure for WF_6, which differ only slightly from those of Kelley /34/.

Temperature, °C.....	-71.4	-56.5	-49.2	-41.5	-33.0	-27.5	-20.3	-10.0	+1.2	17.3
Pressure, mm Hg	1	5	10	20	40	60	100	200	400	760

Barber and Cady /108/ claim that the data of Ruff and Ascher /138/ for the vapor pressures of solid WF_6 obey, fairly accurately, the following equations:

from −8.2 to 2.3° $\log P\,(\text{mm Hg}) = 8.1847 - \frac{1533.1}{T}$;

below −8.2° $\log P\,(\text{mm Hg}) = 10.0682 - \frac{2032.2}{T}$.

Kubaschewski and Evans /27/ give the equation

$$\log P\,(\text{mm Hg}) = -\frac{3040}{T} - 13.09 \log T + 45.60,$$

which is suitable for the calculation of the vapor pressure of liquid WF_6 between the melting and the boiling points.

Heat of transition of WF_6. Barber and Cady /108/ calculated a value of 1600 ± 300 cal/mole from a plot of $\log P$ as a function of T, based on their own experimental results. The same authors calculated the temperature of transition of WF_6 from the data of Ruff and Ascher /138/ for $\log P = f(T)$ and found the value L_{trans} = 2290 cal/mole. Although the last value is of the order of 1600 cal/mole, it is probably too high.

Rossini /51/ considers as the most reliable the value for the heat of transition of WF_6, as reported by Barber and Cady (1600 cal/mole) /108/.

Entropy of transition of WF_6. Rossini /51/ gives the entropy of transition of solid WF_6 as 6.0 cal/deg · mole.

Heat of fusion of WF_6. The heat of fusion of solid WF_6 was determined by Barber and Cady /108/. They calculated this value from the slope of the line $\log P = f\left(\frac{1}{T}\right)$ as 500 ± 100 cal/mole. The same authors /108/ used the data of Ruff and Ascher /138/ and the same method to calculate the heat of fusion of WF_6 as 510 cal/mole.

From vapor pressure data of WF_6 a value of 1800 cal was calculated for the heat of fusion of WF_6 /109/. Kubaschewski and Evans /27/ calculated from this result an approximate value of 500 cal/mole for the [molar] heat of fusion of WF_6. Rossini /51/ also gives the value of 500 cal/mole.

Entropy of fusion of WF_6. The entropy of WF_6 is 1.8 cal/mole · degree /51/.

Heat capacity change of WF_6 during vaporization. The heat capacity change of WF_6 during vaporization is

$$\Delta C_p = -2.6 \text{ cal/degree} \cdot \text{mole}.$$

Heat of vaporization of WF_6. This value was calculated by Barber and Cady /108/ by the Clapeyron equation from their experimental data on vapor pressures of WF_6. The heat of fusion according to these workers is 6150, 5930, 6245 at 25°, 40°, and at the boiling point, respectively.

According to Kelley /34/, the heat of vaporization of WF_6 is 6350 cal/mole at 290.4°K, and 6149 cal/mole at 298°K. Kubaschewski and Evans /27/ give the heats of vaporization of WF_6 at 25° and 17° (boiling point) as 6.15 ± 0.4 kcal/mole and 6.35 ± 0.5 kcal/mole, respectively.

Kelley /34/ gives the following equation for the variation of the heat of vaporization with temperature:

$$L_{vap} = 13{,}900 - 26T \text{ cal/mole}.$$

In the derivation of this equation Kelley /34/ utilized the data of Ruff and Ascher /138/ on the vapor pressure of WF_6.

Entropy of vaporization of WF_6. According to Kelley /34/, the entropy of vaporization is $\Delta S_{290.4}$ = 21.9 cal/degree · mole.

Free energy change of vaporization of WF_6. The free energy change of vaporization of WF_6 is $\Delta F^0_{298} = -166$ cal/mole. ΔF as a function of T is expressed by the following equation /34/:

$$*F^0_T = 13{,}900 + 59.9T \log T - 195.40T.$$

Heat capacity change of WF_6 during sublimation. The change in the heat capacity of WF_6 during sublimation is $\Delta C_p = -12$ cal/deg · mole /34/.

Heat of sublimation of WF_6. According to Kelley /34/, $L_{subl} = 11{,}880 - 12T$, hence L_{298} = 8303 cal/mole.

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* [Probably ΔF^0_T is meant.]

The free energy change of sublimation of WF_6. The free energy change of sublimation of WF_6 is calculated by the equation /24/:

$$F_T^0* = 11{,}880 + 27.6\,T \log T - 109.32T,$$

hence, $\Delta F^0_{298} = -350$ cal/mole.

Entropy of WF_6. Kubaschewski and Evans /27/ give the entropy of gaseous WF_6 as $S^0_{298} = 89.0 \pm 5.0$ cal/degree · mole. The deviation from this value does not exceed 5.5%.

Tungsten dichloride WCl_2 ($M = 254.834$)

Density of WCl_2. According to Biltz and Fendius /110/, the density of WCl_2 at 25° is 5.436 g/cm^3.

Molar volume of WCl_2. The molar volume of WCl_2 is 46.9 cm^3/mole.

Heat and entropy of disproportionation of WCl_2. Shchukarev and co-workers /111/ measured the disproportionation pressure of tungsten dichloride from 490 to 580° by a static method. The results showed that WCl_2 disproportionates and forms gaseous tungsten tetrachloride and tungsten pentachloride according to the following equations:

$$2WCl_2\,(s) = W(s) + WCl_4\,(g) \qquad (1)$$

$$5WCl_2\,(s) = 3W(s) + 2WCl_5\,(g) \qquad (2)$$

From vapor pressure measurements the authors /111/ calculated the following thermodynamic parameters of the disproportionation reaction:

$\Delta H^\circ = 59 \pm 2$ kcal and $\Delta S = 67 \pm 2$ e.u. for reaction (1)

and $\Delta H^\circ = 129 \pm 4$ kcal, and $\Delta S = 145 \pm 4$ e.u. for reaction (2).

Heat of formation of WCl_2. Rossini et al. /51/ give the heat of formation of WCl_2 as $\Delta H^0_{298} = -38$ kcal/mole.

Tungsten tetrachloride WCl_4 ($M = 325.748$)

Density of WCl_4. The density of WCl_4, according to Biltz and Fendius /110/, is 4.624 g/cm^3 at 25°.

Molar volume of WCl_4. The molar volume of WCl_4 is 70.5 cm^3/mole.

Heat and entropy of disproportionation of WCl_4. Tungsten tetrachloride disproportionates according to the following equations:

$$3WCl_4\,(s) = WCl_2\,(s) + 2WCl_5\,(g) \text{ from 300 to 430°,}$$

$$\text{and } WCl_2\,(s) + 2WCl_5\,(g) = 3WCl_4\,(g) \text{ from 450 to 600°.}$$

The heats of these two reactions are 66 ± 4 kcal and 50 ± 4 kcal [per mole], respectively.

The entropy of the first reaction is $\Delta S = 90 \pm 4$ e.u. and is $\Delta S = 60 \pm 4$ e.u. for the second reaction. These data were reported by Shchukarev and co-workers /111/.

Heat of formation of WCl_4. Rossini et al. /51/ give this value as $\Delta H^0_{298} = -71$ kcal/mole.

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* [Probably ΔF°_T is meant.]

Tungsten pentachloride WCl_5 (M = 361.205)

Density of WCl_5. The density of tungsten pentoxide is 3.875 g/cm^3 at 25°, according to Biltz and Fendius /110/.

Molar volume of WCl_5. The molar volume of WCl_5 is 93.3 cm^3/mole.

Melting point of WCl_5. Roscoe /113/ gives the melting point for WCl_5 as 248°. Shchukarev and Novikov /112/ obtained the value of 230± 10° from experimental data on the vapor pressure of WCl_5. Kubaschewski and Evans /27/ consider 244° as the most reliable value. Rossini et al. /51/ give the value of 248°.

Boiling point of WCl_5. Table 35 shows the values obtained by various authors.

TABLE 35

Boiling point of WCl_5

Boiling point, °C	Year	Author	Reference
275.6	1872	Roscoe	/113/
300.0	1924	Voigt, Biltz	/114/
286±2	1956	Shchukarev, Novikov	/112/

Both Kubaschewski and Evans /27/ and Rossini et al. /51/ consider 276° as the most reliable value.

Vapor pressure of WCl_5. Shchukarev and Novikov /112/ determined the vapor pressures of WCl_5 in an apparatus of their own design /115/ equipped with a membrane null-point manometer. Their results are summarized in Table 36.

TABLE 36

Vapor pressure of WCl_5 /112/*

Temperature, °C	Vapor pressure mm Hg	Temperature, °C	Vapor pressure mm Hg	Temperature, °C	Vapor pressure mm Hg
140	4	259	344	253	317
173	21	248	239	264	433
201	64	234	153	276	535
217	87	218	86	278	650
239	220	201	59	283	705
266	444	184	28	285	760
271	536	174	18	273	601
276	582	193	44	264	424
285	718	204	59	250	270
286	760	232	156	215	99
276	565	241	209	140	5

* The results are reported in the order in which they were obtained.

Heat of fusion of WCl_5. The heat of fusion of WCl_5 is approximately L_{fus} = 8.0 kcal/mole /27/.

Heat of vaporization of WCl_5. According to Shchukarev and Novikov /112/, the heat of vaporization of WCl_5 is 15.7 ± 0.5 kcal/mole at

the boiling point (286°). Kubaschewski and Evans /27/ give an approximate value of 12.5 kcal/mole at a boiling point of 270°.

Entropy of vaporization of WCl_5. $\Delta S_{vap} = 28.3 \pm 10$ e.u. /112/.

Heat of sublimation of WCl_5. According to Shchukarev and Novikov /112/, the heat of sublimation of WCl_5 is 16.7 ± 0.5 kcal.

In another work, Shchukarev and co-workers /111/ found the value 18.5 ± 0.5 kcal for the sublimation process $WCl_5(s) \rightarrow WCl_5(g)$ in the temperature range 150 to 253°.

Entropy of sublimation of WCl_5. The entropy of sublimation of WCl_5 has been given as $\Delta S = 30.3$ e.u. /112/ or $\Delta S = 33.1 \pm 0.7$ e.u. /111/.

Heat of disproportionation of WCl_5. Shchukarev and co-workers /111/ found optical-tensometric methods that gaseous tungsten pentachloride disproportionates with formation of gaseous tungsten tetrachloride and tungsten hexachloride.

The disproportionation of tungsten pentachloride, according to the equation $2WCl_5(g) = WCl_6(g) + WCl_4(g)$ in the range 300 to 500°, is accompanied by a heat effect $\Delta H^0_{298} = 6$ kcal /111/.

Entropy of disproportionation of WCl_5. Shchukarev and co-workers /112/ determined the entropy for the disproportionation equation $2WCl_5(g) = WCl_6(g) + WCl_4(g)$ to be $\Delta S^0_{298} = 5$ e.u.

Heat of formation of WCl_5. The heat of formation of WCl_5 $\Delta H^0_{298} = -84$ kcal/mole /51/.

Tungsten hexachloride WCl_6 ($M = 396.662$)

Allotropy of WCl_6. Tungsten hexachloride exists in two allotropic modifications, α and β. The $\alpha \rightleftharpoons \beta$ transition takes place at 226.9°. Rossini and co-workers /51/ report the existence of a third modification of WCl_6 at temperatures below 169°.

Crystal structure of WCl_6. Tungsten hexachloride has a rhombohedric crystal structure with the following lattice parameters: $a = 6.58$ Å and $\alpha = 55°$ /27/.

Density of WCl_6. According to Smith and Exner /88/, the density of WCl_6 at room temperature is 3.518 g/cm^3. Biltz and Fendius give the density of WCl_6 at 25° as 3.520 g/cm^3 /110/.

Molar volume of WCl_6. According to Biltz and Fendius, the molar volume of WCl_6 is 112.7 cm^3/mole /110/.

Temperature of transition of WCl_6. Kubaschewski and Evans /27/ give this value as 227°. According to Ketelaara et al. /116/, the transition point is 226.93 ± 0.3°. Rossini et al. /51/ consider $t_{trans} = 226.9°$ as the best value.

Melting and boiling points of WCl_6. The melting and boiling points of WCl_6 are given in Table 37.

Vapor pressure of WCl_6. The vapor pressure of WCl_6 was measured by Vernon /120/ by means of a flow method. His results are given in the table below.

Temperature, °C	25	50	100	150
Vapor pressure, mm Hg	$5 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$	$1.01 \cdot 10^{-1}$	25.1

Shchukarev and Novikov /112/ found by experiment that the vapor pressure of WCl_6 increases from 43 mm Hg at 215° to 752 mm Hg at 341° (Table 38).

TABLE 37

Melting and boiling points of WCl_6

Melting point	Boiling point	Year	Author	Reference
273	—	1910	Michael, Murphy	/117/
—	347	1924	Voigt, Biltz	/118/
284.0 ± 0.1	336.5	1943	Ketelaara et al.	/116/
284	337	1956	Kubaschewski, Evans	/27/
275 ± 10	348 ± 2	1956	Shchukarev, Novikov	/112/
284 at 233 mm Hg	336.5	1952	Rossini et al.	/51/
—	337	1953	Shchukarev, Novikov	/119/

TABLE 38

Vapor pressure of WCl_6 /112/

Temperature, °C	Vapor pressure, mm Hg	Temperature, °C	Vapor pressure, mm Hg	Temperature, °C	Vapor pressure, mm Hg
215	43	334	621	299	307
265	159	336	669	289	257
280	225	338	706	260	187
299	307	341	752	250	109
310	400	336	638	234	77
317	454	332	488	212	38
322	513	315	410	187	16
329	585	309	354		

According to Rossini /51/, the vapor pressure of WCl_6 is

38 mm Hg at 226.9°
233 mm Hg at 284.0°
760 mm Hg at 336.5°

The vapor pressure of α- and β-WCl_6 in the solid state is given by the following equations:

$$\log P\,(\text{mm Hg}) = -4580\,T^{-1} + 10.73. \quad (\text{from } 425 \text{ to } 500°\text{K})$$

and

$$\log P\,(\text{mm Hg}) = -3840\,T^{-1} + 9.26. \quad (\text{from } 500 \text{ to } 557°\text{K}).$$

The variation of vapor pressure with temperature for liquid tungsten hexachloride from 509 to 635°K is given by the following equation /27/:

$$\log P\,(\text{mm Hg}) = -3330\,T^{-1} + 8.35.$$

Heat of transition of WCl_6. The heat of transition, L_{trans} of $\alpha \rightleftharpoons \beta$ WCl_6, according to Kubaschewski and Evans /27/, is approximately 3.4 kcal/mole. The same value is given by Rossini /51/.

Entropy of transition of WCl_6. Rossini and co-workers /51/ give the entropy of transition, ΔS_{trans}, as 6.8 cal/mole · degree at a transition temperature of 226.9°.

Heat of fusion of WCl_6. Kubaschewski and Evans /27/ and also Rossini and co-workers /51/ give the value of L_{fus} as 2.3 kcal/mole.

Heat of vaporization of WCl_6. Vernon /120/ calculated this value as 1198 cal/mole. According to Kubaschewski and Evans /27/ the heat of vaporization, L_{vap}, of WCl_6 at 337° is 15.2 ± 1.5 kcal/mole.

Shchukarev and Novikov /112/ determined the heat of vaporization of liquid WCl_6 as 12.6 ± 0.5 kcal.

Rossini /51/ gives this value at 336.5° as L_{vap} = 14.9 kcal/mole.

Entropy of vaporization of WCl_6. According to Shchukarev and Novikov /112/, the entropy of vaporization of WCl_6 is 20.4 ± 1.0 e.u. This value was determined from experimental values of vapor pressures. Rossini /51/ considers the best value for the entropy of vaporization of liquid WCl_6 at the temperature 336.5° to be 24.4 cal/mole · degree.

Heat of sublimation of WCl_6. Shchukarev and Novikov /112/ calculated this value from vapor pressure data for WCl_6(s) as L_{subl} = 14.6 ± 0.5 kcal/mole.

Vernon /120/ gives the heat of sublimation of WCl_6, calculated from the vapor pressure of this compound, as 23.8 kcal. Shchukarev and Novikov /119/ investigated the process of sublimation by a gravimetric method in the range 156 to 383° and gave the value 13.7 kcal. This value seems to be the most reliable.

For solid α-WCl_6 Kubaschewski and Evans /27/ give the value L_{subl} = 17.5 ± 1.5 kcal/mole, at a temperature of 226.9° and a pressure of 38 mm Hg. Rossini and co-workers /51/ give the value L_{subl} = 21.0 kcal/mole [for the same modification under the same conditions]. According to these authors the heat of sublimation for β-WCl_6 at 284° and 233 mm Hg is 17.4 kcal/mole.

Entropy of sublimation of WCl_6. The entropy of sublimation of solid WCl_6, as calculated by Shchukarev and Novikov, is 24.2 ± 1.0 e.u. This value was calculated from vapor pressure results. In another study /119/, Shchukarev and Novikov used a gravimetric method for the study of the sublimation of WCl_6 and determined the entropy of this compound as 22.5 e.u.

According to Rossini /51/, the sublimation of α-WCl_6 is accompanied by an entropy change, ΔS_{subl}, of 42.0 cal/mole · degree at 226.9°. The corresponding entropy change for β-WCl_6 is 31.2 cal/mole · degree at 284°.

Heat of dissociation of WCl_6. The heat of dissociation of WCl_6 from 1087 to 1727° is 9000 cal/mole. The values of the partial pressure of Cl_2 and the equilibrium constants $K = \frac{P^3_{Cl_2}}{P_{WCl_6}}$ for the dissociation of this compound are given in Table 39 /120/.

TABLE 39

Dissociation of WCl_6
(Partial pressure of Cl_2 and equilibrium constant)

Temperature, °C	Partial pressure, mm Hg	Equilibrium constant K
1087	$3.68 \cdot 10^{-5}$	$2.3 \cdot 10^{-8}$
1227	$1.67 \cdot 10^{-4}$	$2.1 \cdot 10^{-6}$
1327	$4.08 \cdot 10^{-4}$	$2.6 \cdot 10^{-5}$
1727	$1.64 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$

Heat of formation of WCl_6. The standard heat of formation, ΔH^0_{298}, of WCl_6, is given as −97.0 ± 4.0 kcal/mole, according to Kubaschewski and Evans /27/, and as −98.7 kcal/mole, by Rossini et al. /51/.

Tungsten bromides

There is very few thermodynamic data available on the bromides of tungsten. Rossini /51/ reports the melting point and boiling point of WBr_5 as 276 and 333°, respectively, and also the heats of formation ΔH^0_{298} for WBr_2, WBr_4, WBr_5, and WBr_6 from elements. These values are given below:

	ΔH^0_{298}, kcal/mole
WBr_2	19
WBr_4	35
WBr_5	42
WBr_6	44

Tungsten iodides

As with the bromides of tungsten, there are very few thermodynamic data on the iodides of tungsten. The data of Rossini /51/ on the heats of formation of solid tungsten iodides from the elements are quoted below

	ΔH^0_{298}, kcal/mole
WI_2	-1
WI_4	0
WI_5	+27

5. CARBIDES OF TUNGSTEN

Tungsten carbide W_2C (M = 379.851)

Density of W_2C. Becker /121/ calculated from X-ray data the density of this compound at room temperature and obtained the value 17.15 g/cm^3.

Molar volume of W_2C. According to Becker /121/, the molar volume of W_2C is 22.1 cm^3/mole.

Hardness of W_2C. W_2C is harder than corundum (it scratches corundum).

Temperature of transition of W_2C. Tungsten carbide W_2C is converted from the α- to the β-modification at 2300 — 2400°.

Melting point of W_2C. Table 40 shows the melting point of W_2C according to various workers.

TABLE 40

Melting point of W_2C

Temperature, °K	Year	Author	Reference
3150	1921	Andrews, Duschman	/122/
3000 ± 15	1929	Barnes	/123/
3130	1930	Agte, Alterthum	/124/
3130	1949	Greenwood	/125/
3130	1952	Rossini et al.	/ 51/

Tungsten monocarbide WC (M = 195.931)

Crystal structure of WC. Tungsten monocarbide has a hexagonal structure. The lattice parameters are a = 2.90 Å and b = 2.84 Å.

Density of WC. Values for the density of WC, according to various authors, vary from 15.5 to 15.7 g/cm^3. The density of WC, as determined by X-ray measurements, is 15.77 g/cm^3.

Hardness of WC. The hardness of WC is 9 units on the Mohs hardness scale.

Melting point of WC. The phase diagram of WC was thoroughly investigated. WC melts with decomposition at 2600°. Total fusion of the alloy corresponding to the composition WC occurs approximately at 2800° /126/.

The melting point of WC is 2877°, according to Friedrich and Sittig /127/, and 2866.8°, according to Agte and Alterthum /124/. Kubaschewski and Evans /27/ showed that tungsten monocarbide decomposes when heated to the melting point. Rossini and co-workers /51/ give the value of 2857° for the melting point of WC.

Heat capacity of WC. Kubaschewski and Evans give the following equation for the variation of the heat capacity with temperature from 298 to 3000°K.

$$C_p\,(\text{cal/degree}\cdot\text{mole}) = 7.98 + 2.17 \times 10^{-3} T.$$

The accuracy of this equation is 6%.

Entropy of WC. $S^\circ_{298} = 8.5 \pm 1.5$ cal/degree · mole /27/.

Heat of formation of WC. The values for the heat of formation of WC are given in Table 41.

TABLE 41

Heat of formation of WC

Heat of formation $-\Delta H$, kcal/mole	Year	Author	Reference
8.41 ± 0.19	1948	Huff et al.	/101/
9.1 ± 2.5	1956	Kubaschewski, Evans	/ 27/
8.4	1956	Samsonov	/128/
9.09	1952	Rossini et al.	/ 51/

Free energy of formation of WC. The free energy of formation of WC from its elements can be calculated by the following equation proposed by Kubaschewski and Evans /27/:

$$\Delta F_T = -9100 + 0.4T.$$

The temperature range of this equation is 298 to 2000°K, and its accuracy is not less than ± 3 kcal.

6. THERMODYNAMICS OF TUNGSTEN. OXIDATION AND REDUCTION REACTIONS OF TUNGSTEN COMPOUNDS

The heterogeneous equilibria ($WO_3 + H_2$) and ($WO_3 + CO$) were studied by Wöhler and Günther /129/, Van Liempt /80/, Reinders and Vervloet /130/,

Shibata, Wöhler, and Kunst /81, 131/, and others. The main object of these studies was the determination of the equilibrium and the investigation of phase change on the reduction isotherms of WO_3. The equilibrium constants, K_p, however, were not determined by sufficiently accurate methods and the authors /129, 80, 130, 81, 131/ did not take into account the variation of the heat capacity of WO_3 with temperature. As a result, the values obtained for K_p show differences which may be as high as 40%.

Moreover, the authors did not identify by X-ray methods either the initial reactant WO_3, or the intermediate oxides $WO_{2.90}$ and $WO_{2.72}$, formed as a result of reduction of WO_3. This is one of the causes of the wide discrepancies of the data.

Thus, Shibata /81/, when studying the equilibrium of tungsten oxides with a mixture of $CO_2 + CO$, erroneously assumed the reaction equation as $2WO_3 + CO \rightleftharpoons W_2O_5 + CO_2$ and calculated the thermodynamic parameters for W_2O_5. Later investigations did not confirm the existence of this compound.

Wöhler and Günther /129/, Shibata /81/, Reinders and Vervloet /130/, and other authors observed in the study of the reaction ($WO_3 + H_2$) three stages of reduction:

$$\left.\begin{array}{l} 1)\ 2WO_3 + H_2 = W_2O_5 + H_2O, \\ 2)\ W_2O_5 + H_2 = 2WO_2 + H_2O, \\ 3)\ \frac{1}{2}WO_2 + H_2 = \frac{1}{2}W + H_2O. \end{array}\right\} (A)$$

Nakaon /141/, Smithells /142/, Liempt /143/ give somewhat different equations for this reduction:

$$\left.\begin{array}{l} 1)\ 4WO_3 + H_2 = W_4O_{11} + H_2O, \\ 2)\ \frac{1}{3}W_4O_{11} + H_2 = \frac{4}{3}WO_2 + H_2O, \\ 3)\ \frac{1}{2}WO_2 + H_2 = \frac{1}{2}W + H_2O. \end{array}\right\} (B)$$

Schenk and Dingman /144/ studied the reduction equation ($WO_3 + CO$) and attributed the formula W_3O_8 to the intermediate oxide.

Funaki and Acada /145/ observed seven stages of reduction of tungsten trioxide:

$$\left.\begin{array}{l} 1)\ 4WO_3 + H_2 = W_4O_{11} + H_2O, \\ 2)\ W_4O_{11} + H_2 = 2W_2O_5 + H_2O, \\ 3)\ 2W_2O_5 + H_2 = W_4O_9 + H_2O, \\ 4)\ W_4O_9 + H_2 = 4WO_2 + H_2O, \\ 5)\ 2WO_2 + H_2 = W_2O_3 + H_2O, \\ 6)\ W_2O_3 + H_2 = 2WO + H_2O, \\ 7)\ WO + H_2 = W + H_2O. \end{array}\right\} (C)$$

The equilibrium constant obtained by Wöhler and Günther /129/ and the variation of log K_p with temperature are presented in Table 42.

TABLE 42

Variation of K_p with temperature for the three stages of reduction of WO_3 by hydrogen according to Wöhler and Günther, /129/

$2WO_2+H_2=W_2O_5+H_2O$		$W_2O_5+H_2=2WO_2+H_2O$		$\frac{1}{2}WO_2+H_2=\frac{1}{2}W+H_2O$	
Temperature, °K	$K_{p_{det}}$	Temperature, °K	$K_{p_{det}}$	Temperature, °K	$K_{p_{det}}$
973	6.5	989	1.57	972	0.405
1075	8.95	1078	1.96	1075	0.610
1172	12.1	1175	2.31	1206	0.950
1182	11.5	1282	2.63	1264	1.080
		1318	2.90	1344	1.400
$\log K_{p_1} = -\frac{1375}{T} + 2.235$		$\log K_{p_2} = -\frac{1000}{T} + 1.218$		$\log K_{p_3} = -\frac{1904}{T} + 1.554$	

The data of Table 42 were obtained by Wöhler and Günther in 1923, 14 years after Wöhler had started his studies on the reduction of tungsten oxides by hydrogen (1909).

In 1932, Wöhler, Shibata, and Kunst /131/ began a new study of the reduction system ($WO_3 + H_2$). The method used was that of free diffusion. The apparatus was described previously /129/. They attempted to avoid the errors of their earlier work (1923) where owing to a short holding time true equilibrium was not attained. The first reduction stage was between 700 and 800°C, the second between 700 and 920°C, and the third between 700 and 1050°C. These authors derived the following $\log K_p - \frac{1}{T}$ equations for the second and third stages of the reduction, respectively:

$$\log K_{p_2} = -\frac{850}{T} + 1.059;$$

$$\log K_{p_3} = -\frac{1917}{T} + 1.56.$$

These equations differ only slightly from those obtained by Wöhler and Günther in their earlier work /129/. The experiments were performed very carefully. The flaws in this method were apparently those inherent in the static method; also, no X-ray studies of WO_3 or its reduction products were conducted.

Chaudron /146/ studied the reaction ($WO_3 + H_2$) at lower temperatures (~400°) than Wöhler et al. /129, 131/. Chaudron /146/, like Wöhler and Günther /129/, observed three stages of reduction of WO_3. On the basis of the data of Chaudron /146/, Van Liempt /143/ derived the following equations for each reduction stage:

$$\log K_{p_1} = -\frac{2468}{T} + 3.15;$$

$$\log K_{p_2} = -\frac{817}{T} + 0.80;$$

$$\log K_{p_3} = -\frac{1111}{T} + 0.845.$$

For the sake of comparison, Table 43 shows the values for the three stages of reduction of WO_3 by hydrogen at 973, 1073, 1173, and 1273°K. These values were determined from the linear equation of log K_p as a function of $\frac{1}{T}$ which Van Liempt /143/ derived from the data of Chaudron /146/, and also from those calculated from the equations of Wöhler and Günther /129/ and of Wöhler, Shibata, and Kunst /131/.

TABLE 43

Variation of K_p with temperature, according to various workers /143, 146, 129, 131/, for the three stages of reduction of WO_3 by hydrogen

Stage	Temperature, °K				Author	Reference
	973	1073	1173	1273°		
	K_p					
First	4.1	7	11	16.3	Chaudron	/146/
	6.5	8.95	12.10	14.3	Wöhler, Günther	/129/
	—	—	—	—	Wöhler, Shibata, Kunst	/131/
Second	1.10	1.31	1.53	1.72	Chaudron	/146/
	1.55	1.96	2.31	2.71	Wöhler, Günther	/129/
	1.53	1.85	2.16	2.46	Wöhler, Shibata, Kunst	/131/
Third	0.50	0.63	0.79	0.94	Chaudron	/146/
	0.39	0.61	0.85	1.14	Wöhler, Günther	/129/
	0.39	0.59	0.84	1.13	Wöhler, Shibata, Kunst	/131/

It can be seen from this table that the results of Wöhler, Shibata, and Kunst /131/ and those of Wöhler and Günther /129/ show good agreement (differences of 4 — 5%), whereas those of Chaudron /146/ show differences which sometimes reach 40%.

Funaki and Acada /145/ studied the reduction of WO_3 with hydrogen by the method of continuous weighing of the reduced oxide. In this investigation six lower oxides of tungsten were found, namely: W_4O_{11}, W_2O_5, W_4O_9, WO_2, W_2O_3, and WO. These authors /145/ obtained two reduction isotherms of tungsten trioxide at 870 and 700°. Table 44 shows the equilibrium constants, calculated by the authors /145/ from data on the reduction of WO_3 with hydrogen at 700°. For comparison, this table also contains the equilibrium constants of Wöhler /129, 131/ (reaction scheme A), and those of Smithells /142/ (reaction scheme B). In addition, the table also shows the equations for $\log K_p = f\left(\frac{1}{T}\right)$ for the reduction reaction ($WO_3 + H_2$) as determined by Funaki and Acada /145/ (reaction scheme C).

It can be seen from Table 44 that the experimental equilibrium constants, obtained by Funaki and Acada /145/ for one stage (particularly the second), sometimes show discrepancies greater than 35%. For this reason the equations derived by these authors for the variation of $\log K_p$ with T appear to be

somewhat inaccurate. Despite, therefore, their very interesting method of investigation, the values obtained by these authors for the equilibrium constants cannot be used for calculation of the thermodynamic functions of the oxides of tungsten.

TABLE 44

K_p as a function of T for the reduction of WO_3 with hydrogen, according to Wöhler /129, 131/, Smithells /142/, and Funaki and Acada /145/

Composition of oxides corresponding to phase changes	K_p det, according to Funaki and Acada /145/	K_p av, according to Funaki and Acada /145/	K_p det, according to Wöhler et al. /129, 131/	K_p det, according to Smithells /142/	Equations for $\log K_p = f\left(\frac{1}{T}\right)$ according to Funaki and Acada /145/
WO_3 ↓ W_4O_{11}	6.06 6.58 5.75 6.39	$K_{p_1}=6.115$	$K_{p_1}=4.82$	$K_{p_1}=6.115$	$\log K_{p_1} = -\frac{1933}{T}+2.765$
↓ W_2O_5	3.55 2.67 2.50 2.33	$K_{p_2}=3.49$		$K_{p_2}=2.73$	$\log K_{p_2} = -\frac{798.5}{T}+1.398$
↓ W_4O_9	2.45 2.30	$K_{p_3}=2.45$	$K_{p_2}=2.35$		$\log K_{p_3} = -\frac{596}{T}+0.46$
↓ WO_2	2.28 2.19	$K_{p_4}=2.26$			$\log K_{p_4} = -\frac{117.2}{T}+0.474$
↓ W_2O_3	1.29 0.456 0.544	$K_{p_5}=0.667$			$\log K_{p_5} = -\frac{1810}{T}+1.523$
↓ WO	0.379 0.370	$K_{p_6}=0.370$	$K_{p_3}=0.579$	$K_{p_3}=0.519$	$\log K_{p_6} = -\frac{2383}{T}+1.989$
↓ W	—	$K_{p_7}=0.355$			$\log K_{p_7} = -\frac{2352}{T}+1.955$

In the past few years, the heterogeneous equilibria of the reaction WO_3 + H_2 were studied by Gerasimov, Vasil'eva, and Simanov /76, 94, 95, 132/ and also by Griffis /75, 79/.

When calculating the thermodynamic parameters of tungsten oxides, Gerasimov, Vasil'eva, and Simanov /76, 94, 95, 132/ took into account the effect of thermal diffusion on the experimental determination of the equilibrium constant K_p, the variation with temperature of the heat capacity of the tungsten trioxide undergoing reduction, and the structure of the initial WO_3 samples. For this reason, the results of the thermodynamic parameters of the tungsten oxides, calculated by Vasil'eva, Gerasimov, and Simanova /76, 94/, are much more accurate than those of Wöhler and Günther /129/, Van Liempt /80/, and others.

The equilibria α- and β-$WO_3 + H_2$ /76, 94, 95, 132/

The equilibria of α-$WO_3 + H_2$ and β-$WO_3 + H_2$ were determined in the temperature ranges 640 to 937° and 600 to 791°, respectively, by the flow method. The investigations were carried out, essentially, by reduction. The reduction proceeds in four stages (see Gerasimov, Vasil'eva, and Simanov /76, 94, 95, 132/):

$$10WO_3(\alpha,\beta) + H_2 = 10WO_{2.90} + H_2O, \quad \text{(I)}$$

$$\frac{50}{9}WO_{2.90} + H_2 = \frac{50}{9}WO_{2.72} + H_2O, \quad \text{(II)}$$

$$\frac{50}{36}WO_{2.72} + H_2 = \frac{50}{36}WO_2 + H_2O, \quad \text{(III)}$$

$$\frac{1}{2}WO_2 + H_2 = \frac{1}{2}W + H_2O. \quad \text{(IV)}$$

For the four stages of reduction of β-WO_3 by hydrogen the mean values of the equilibrium constant K_p were obtained. These values are given in Table 45.

TABLE 45

Average values of equilibrium constants of the reduction of tungsten oxides by hydrogen

I Stage		II Stage	
T, °K	$K_{p_{av}}$	T, °K	$K_{p_{av}}$
903	2.78	873	0.8978
965	4.73	903	1.29
1023	7.73	918	1.59
		961	2.60
		965	2.78
		1023	4.91
		1064	7.64

The equilibrium constants of the reduction of α-WO_3 in the range 640 to 937°, and of β-WO_3 in the range 630 to 791°, are given below.

Equilibrium of the reaction (α-$WO_3 + H_2$), 640 to 937°

1) $\log K_{p_I} = -\frac{3792.0}{T} + 4.8268,$

2) $\log K_{p_{II}} = -\frac{1442.5}{T} + 1.684,$

3) $\log K_{p_{III}} = -\frac{801.7}{T} + 0.8615,$

4) $\log K_{p_{IV}} = -\frac{2219.0}{T} + 1.5809.$

The mean experimental error range for the first two equations is ±3%, for the third ±1.5%, and for the fourth ±1%.

Equilibrium of the reaction (β-$WO_3 + H_2$), 630 to 791°

$$1)\ \log K_{p_I} = -\frac{3266.9}{T} + 4.0667,$$

$$2)\ \log K_{p_{II}} = -\frac{4508.5}{T} + 5.10866,$$

$$3)\ \log K_{p_{III}} = -\frac{904.83}{T} + 0.90642,$$

$$4)\ \log K_{p_{IV}} = -\frac{2325}{T} + 1.650.$$

The mean error of the first two equations is within 2%, while that of the second two is within 0.6%.

The authors combined the reactions of the four stages of reduction and obtained equations for the equilibrium constants and for the free energy for complete reduction according to the equation:

$$\alpha\text{-}WO_3 + 3H_2 \rightleftarrows W + 3H_2O \qquad (V)$$

$$I + II + III + IV = V:$$

$$0.1 \log K_{p_I} + 0.18 \log K_{p_{II}} + 0.72 \log K_{p_{III}} + 2K_{p_{IV}} = \log K_{p_V};$$

$$V.\ \log K_{p_V} = -\frac{5654}{T} + 4.56$$

hence,

$$\Delta F^{\circ}_{T.V} = 25{,}870 - 20.89T.$$

The mean error of the last equation is within ±0.5%.

$$\beta\text{-}WO_3 + 3H_2 = W + 3H_2O; \qquad (5)$$

$$1) + 2) + 3) + 4) = 5:$$

$$0.1 \log K_{p_I} + 0.18 \log K_{p_{II}} + 0.72 \log K_{p_{III}} + 2 \log K_{p_{IV}} = \log K_{p_V};$$

$$5)\ \log K_{p_V} = -\frac{6439}{T} + 5.27884$$

hence,

$$\Delta F^{\circ}_{T.V} = 29{,}458 - 24.15T.$$

The mean error of the last equation is within 0.5%.

Table 46 shows the rounded-off values of the free energy of formation $\Delta F^{\circ}_{T.V}$ for the reduction of the α- and β-modification.

TABLE 46

Free energy of the reduction of α-WO_3 and β-WO_3 with hydrogen

Temperature, °K	Free energy $\Delta F^{\circ}_{T.V}$, kcal/mole	
	α - $WO_3 + H_2$	β - $WO_3 + H_2$
873	7.60	8.37
923	6.60	7.10
1023	4.50	4.70
1064	3.60	3.75
1073	3.45	3.50
1173	1.40	1.10

Vasil'eva, Gerasimov, and Simanov /94, 95/ used the data of Chipman /133/ for the formation of water vapor to calculate the free energy of formation ΔF of α- and β-WO_3 from their elements.

$$H_2 + \frac{1}{2}O_2 = H_2O. \qquad \text{(VI)}$$

$$\text{VI. } \Delta F^\circ_{T.VI} = -59{,}251 + 0.871T \ln T - 0.0_475T^2 + \frac{40{,}800}{T} + 6{,}8085T.$$

Combining $\Delta F^\circ_{T.V}$ and $\Delta F^\circ_{T.VI}$,

$$W + \frac{3}{2}O_2 = \alpha\text{-}WO_3;$$

$$W + \frac{3}{2}O_2 = \beta\text{-}WO_3 \qquad \text{(VII)}$$

$$\text{VII. } \Delta F^\circ_{T.VII} = 3\Delta F^\circ_{T.VI} - \Delta F^\circ_{T.V}.$$

The values of ΔF^0_T for the reaction (VI) $H_2 + \frac{1}{2}O_2 = H_2O$ and (VII) $W + \frac{3}{2}O_2 = \alpha$-$WO_3$, at the temperatures of the experiment, are given in Table 47, and for the reaction (VII) $W + \frac{3}{2}O_2 = \beta$-$WO_3$ in Table 48.

TABLE 47

Free energy of formation of $3H_2O$ and α-WO_3

Temperature, T, °K	Free energy of formation	
	$3H_2O$	α-WO_3
	$-3\Delta F^\circ_T$ VI kcal/mole	ΔF°_T VII kcal/mole
873	143.23	150.8
927	141.30	147.9
1023	137.37	141.9
1073	135.39	138.9
1173	131.49	132.8
1232	128.98	129.0

TABLE 48

Free energy of formation of β-WO_3

Temperature, T, °K	Free energy of formation of β-WO_3
	ΔF°_T VII kcal/mole
873	151.87
903	149.725
965	145.80
1023	142.115
1064	139.51

In the calculation of the free energy of β-WO_3 the following forms of the $C_P = f(T)$ reactions were used:

for O_2 $C_P = 7.52 + 0.81 \cdot 10^{-3}\,T - \frac{0.90 \cdot 10^5}{T^2}$ /134/;

for W $C_P = 5.65 + 0.866 \cdot 10^{-3}\,T$ /134/;

for β-WO_3 $C_P = 16.356 + 10.67 \cdot 10^{-3}\,T$ /92/.

Using the method of Temkin and Shvartsman /135/, which obviates the necessity of calculations, the integration constant J and ΔH in the equation $\Delta F^\circ_T = f(T)$, Vasil'eva, Gerasimov, and Simanov /94, 95/ calculated thermodynamic parameters for the formation of α- and β-WO_3 from their elements according to the equations $W + \frac{3}{2}O_2 = \alpha$-$WO_3$ and $W + \frac{3}{2}O_2 = \beta$-$WO_3$, under standard conditions:

$$W + \frac{3}{2}O_2 = \alpha\text{-}WO_3; \qquad W + \frac{3}{2}O_2 = \beta\text{-}WO_3;$$

$\Delta H^\circ_{298} = -203.0$ kcal/mole; $\Delta H^\circ_{298} = -205.3$ kcal/mole;

$\Delta F^\circ_{298} = -184.7$ kcal/mole; $\Delta F^\circ_{298} = -186.2$ kcal/mole;

$\Delta S^\circ_{298} = -61.6$ cal/mole · deg; $\Delta S^\circ_{298} = -63.9$ cal/mole · deg;

$\Delta S^\circ_{298} = 20.0$ e. u.; $\Delta S^\circ_{298} = 17.6$ e. u.

For the reaction $W + \frac{3}{2}O_2 = \alpha\text{-}WO_3$, the variation of ΔF°_T with T is given by the equation

$$\text{VIII. } \Delta F^\circ_T = -203{,}000 + 61.6T - (-0.574M_0 + 8.589 \cdot 10^{-3}M_1 + 1.35 \cdot 10^{-6}M_{-2}).$$

For the reaction $W + \frac{3}{2}O_2 = \alpha\text{-}WO_3$

$$8)\ \Delta F^\circ_T = -205.3 + 63.9T - (0.574M_0 - 0.8586 \cdot 10^{-3}M_1 - 1.35 \cdot 10^{5}M_{-2}),$$

where M_0, M_1 and M_{-2} are coefficients, the numerical values of which are given for different temperatures in the table of Temkin and Shvartsman /135/.

The ΔF°_T values calculated from equations (VIII) and (8) for certain temperatures are presented in Tables 49 and 50, respectively.

TABLE 49

Free energy of formation of α-WO_3 calculated from equation (VIII)

Temperature, T, °K	Free energy $-\Delta F^\circ_T$, kcal/mole
873	151.0
923	148.0
1023	142.6
1073	139.8

TABLE 50

Free energy of formation of β-WO_3 calculated from equation (8)

Temperature, T, °K	Free energy $-\Delta F^\circ_T$, kcal/mole
298	186.20
673	162.95
873	151.10
965	145.63
1073	139.49
1273	128.20

TABLE 51

Variation of the free energies of formation $-\Delta F^\circ_{T\,1}$ of $\frac{1}{2}WO_2$ with temperature

Temperature, °K	Free energy of formation, kcal	
	$-\Delta F^\circ_{T\,1}$	$-\Delta F_{T\,1}$
973	48.8 ± 1.5	49.5
1073	47.0 ± 1.5	47.5
1173	45.2 ± 1.5	45.4
1273	43.3 ± 1.5	43.3

The values for ΔF_T^0 of Table 49 do not differ from those of Table 47 by more than 0.5% and the values of Table 50 agree with those of Table 48 within 0.3%.

Thus, the equilibrium constants of the reduction of tungsten oxides by hydrogen permit calculation of the thermodynamic functions of the formation of WO_3 from its elements.

However, since the high values of equilibrium constants cannot be measured with sufficient accuracy, and since that accuracy depends on the values calculated for water vapor, the thermodynamic functions of the formation of tungsten oxides from their elements must be independently determined.

For the reaction

$$\frac{1}{2}W + \frac{1}{2}O_2 = \frac{1}{2}WO_2$$

Gerasimov et al. /76/, by the use of emf methods, derived equation

$$\Delta F^\circ_{T_I} = -68{,}542 - 7.21T \log T +$$
$$1.26 \cdot 10^{-3}T^2 - 0.47 \cdot 10^5 T^{-1} + 40.62T \text{ cal},$$

which is valid for experimental data in the temperature range 943 to 1230°K.

The values for $\Delta F^0_{T,I}$, calculated according to this equation over the temperature range 973 to 1273°K, and also those for $\Delta F^0_{T,I}$, calculated by Vasil'eva, Gerasimov, and Simanov /132/ from equilibrium data for reaction (I) for the same temperatures, are shown in Table 51.

For the reaction

$$\frac{100}{72}WO_2 + \frac{1}{2}O_2 = \frac{100}{72}WO_{2.72} \qquad \text{(II)}$$

$$\Delta F^\circ_{T_{II}} = -65{,}300 - 7.21T \log T +$$
$$1.26 \cdot 10^{-3}T^2 - 0.47 \cdot 10^5 T^{-1} + 39.93T \text{ cal}.$$

This equation governs data from 900 to 1173°K. The values of $\Delta F^0_{T,II}$, calculated from this equation in the range 923 to 1173°K, and the values of $\Delta F'_{T,II}$ for reaction (II), calculated by Vasil'eva, Gerasimov, and Simanov /132/ from equilibrium data, are shown in Table 52.

TABLE 52

Variation of the free energies of formation $-\Delta F^\circ_{T\,V}$ and $\Delta F^{\circ\prime}_{T\,II}$ of $\frac{100}{72}W_{2.72}$ with temperature

Temperature, °K	Free energy of formation, kcal	
	$-\Delta F_{T\,II}$	$-\Delta F'_{T\,II}$
923	47.1 ± 0.5	47.2
1023	45.4 ± 0.5	45.4
1123	43.7 ± 0.5	43.6
1173	42.8 ± 0.5	42.7

Combination of the solutions of equations (I) and (II) results in the equation

$$\Delta F^\circ_{T_{III}} = -184{,}106 + 9.23T \log T + 3.43 \cdot 10^{-3}T^2 - 1.28 \cdot 10^5 T^{-1} + 109.9T.$$

for the reaction

$$W + 1.36O_2 = WO_{2.72} \qquad \text{(III)}$$

Gerasimov et al. /76/ used the heat capacities of O_2 and W, given by Britske et al. /136/, in his calculation of the standard thermodynamic parameters. The heat capacity of WO_2 was calculated by the expression $C_p = 17.83 + 1.89 \cdot 10^{-3} T - 3.342 \cdot 10^5 T^{-2}$ with an accuracy of ±3%.

Using these values for the reaction $W + O_2 = WO_2$ Gerasimov et al. /76/ obtained the equation

$$\Delta F_T^\circ = -136.6 - T(4.66M_0 + 0.21M_1 - 2.44M_{-2}) + 41.7T$$

where M_0, M_1, and M_2 are the coefficients of the Temkin-Shvartsman equation /135/.

Hence,

$$\Delta H_{298}^\circ = -136.6 \pm 2 \text{ kcal/mole};$$

$$\Delta S_{298}^\circ = -41.7 \pm 1.5 \text{ e.u.};$$

$$\Delta F_{298}^\circ = -124 \pm 2 \text{ kcal/mole}.$$

Gerasimov et al./76/, using the value of /77/ for S_{298}^0 of W and that of Kelley /61/ for O_2, obtained the result $S_{298}^0 = 15.0 \pm 1.5$ e.u. for WO_2.

Griffis /75, 79/ carried out an exhaustive research on the thermodynamic parameters of reduction of tungsten oxides with hydrogen. His results, using the static equilibrium method at temperatures of 500 to 1000°, have been published /75/.

$$\frac{1}{2}WO_2 + H_2 \rightleftarrows \frac{1}{2}W + H_2O.$$

Equilibrium was attained both for reduction and oxidation. Equilibrium data for reaction $\frac{1}{2}WO_2 + H_2 \rightleftarrows \frac{1}{2}W + H_2O$ are reported in Table 53.

TABLE 53

Variation of the equilibrium constant $K_p = \frac{P_{H_2O}}{P_{H_2}}$ with temperature for reaction $\frac{1}{2}WO_2 + H_2 \rightleftarrows \frac{1}{2}W + H_2O$ /75/

Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Original conditions	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Original conditions
500	0.112	Reduction	800	0.460	Reduction
500	0.118	"	800	0.460	"
500	0.120	Oxidation	800	0.515	Oxidation
500	0.121	"	800	0.520	Reduction
500	0.120	Reduction	800	0.510	Oxidation
600	0.214	"	900	0.694	"
600	0.212	"	900	0.684	Reduction
600	0.210	Oxidation	900	0.705	Oxidation
600	0.208	Reduction	900	0.690	Reduction
600	0.218	Oxidation	900	0.709	Oxidation
600	0.206	"	900	0.695	Reduction
700	0.356	"	1000	0.931	"
700	0.346	Reduction	1000	0.935	"
700	0.348	Oxidation	1000	0.935	Oxidation
700	0.340	"	1000	0.945	"
700	0.351	Reduction	1000	0.937	"
700	0.355	"	1000	0.934	Reduction
800	0.507	"			

The heat capacity change ΔC_P for the reaction $WO_2 + 2H_2 \rightarrow W + 2H_2O$ in the range 500 to 1000° was calculated from the literature for the heat capacities of H_2, H_2O /27/, W /139/, and from C_P = 14.0 cal/deg · mole for WO_2:

$$\Delta C_p = 6.98 + 4.32 \cdot 10^{-3} T - 0.08 \cdot 10^5 T^{-2}.$$

Using the methods of Σ-functions and least squares, the following equations were obtained from the equilibrium data of Table 53 and from ΔC_P.

$$\Delta H_T^\circ = 21{,}000 - 6.96T + 2.16 \cdot 10^{-3} T^2 + 0.08 \cdot 10^5 \cdot \frac{1}{T}.$$

$$\Delta F_T^\circ = 21{,}000 + 6.96T \ln T - 2.16 \cdot 10^{-3} T^2 + \frac{0.04 \cdot 10^{-5}}{T} - 63.1T.$$

From these equations the values ΔH^0_{298} = 19.4 ± 0.2 kcal/mole and ΔF^0_{298} = 13.9 ± 0.2 kcal/mole were calculated.

From the above values for ΔF^0_{298} and ΔH^0_{298} /27/ the heat contents and the free energy for the reaction $W + O_2 = WO_2$ were also calculated and the following values obtained: ΔH^0_{298} = −135.0 ± 0.3 kcal/mole and ΔF^0_{298} = −123.1 ± 0.3 kcal/mole. The heat of formation of WO_2 was also obtained by direct combustion in a bomb calorimeter. The same method also served for the determination of the heat of combustion of WO_3, $WO_{2.72}$, and $WO_{2.90}$. The heat of formation of WO_3 as determined by calorimetric measurements /59/ is given below:

	$-\Delta H^\circ_{298}$, kcal/mole
$W + \frac{3}{2} O_2 \rightarrow WO_3$	199.5 198.5 199.1
$WO_2 + \frac{1}{2} O_2 \rightarrow WO_3$	62.0 61.4 60.8 62.3
$WO_{2.72} + \frac{0.28}{2} O_2 \rightarrow WO_3$	15.0 16.2 17.1 15.8
$WO_{2.90} + \frac{0.10}{2} O_2 \rightarrow WO_3$	4.7 5.9 6.2 6.4

These data were used for the calculation of the heats of formation of tungsten oxides. The corresponding ΔH^0_{298}'s are shown in Table 54.

The individual standard entropies of W and O_2 /140/ were utilized to calculate the standard entropy of WO_2, S^0_{298} = 17.1 ± 1.0 e.u.

Griffis /79/ also gives the thermodynamic parameters obtained from an exhaustive study of the heterogeneous equilibrium ($WO_3 + H_2$) by the static equilibrium method in an improved apparatus. Griffis noted /79/ that his earlier measurements /75/ were not sufficiently accurate, since he did not take into account the effect of thermal diffusion. The data in /75/* are more accurate and were used to calculate the standard heats of formation and entropies of the solid oxides WO_2, $WO_{2.72}$, $WO_{2.90}$, and WO_3.

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* [Probably /79/ is intended.]

TABLE 54

Heats of formation of tungsten oxides /75/

Oxide	Heat of formation, $-\Delta H^{\circ}_{298}$, kcal/mole	Method of determination	Value of $-\Delta H^{\circ}_{298}$, according to reference
WO_3	199 ± 1	Combustion	200.2 ± 0.10 /101/
WO_2	137 ± 1	"	135 /71/
WO_2	135.0 ± 0.3	Equilibrium	134 ± 2 /71/
$WO_{2.72}$	183 ± 1	Combustion	—
$WO_{2.90}$	193 ± 1	"	—

All data were obtained by alternative reduction and oxidation and are summarized in Tables 55 — 58.

TABLE 55

Variation of the equilibrium constant $K_p = \frac{P_{H_2O}}{P_{H_2}}$ with temperature for the system $WO_3 - H_2 - WO_{2.90} - H_2O$

Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$
600	2.30	700	5.10	800	8.40
600	2.21	700	4.91	800	9.20
600	2.39	700	5.30	800	9.61
600	2.28	700	5.24	800	9.12
600	2.25	700	5.05	800	9.61
600	2.32	700	5.12	800	9.54

TABLE 56

Variation of the equilibrium constant $K_p \frac{P_{H_2O}}{P_{H_2}}$ with temperature for the system $WO_{2.90} - H_2 - WO_{2.72} - H_2O$

Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$
600	1.20	700	3.20	800	7.20
600	1.25	700	3.10	800	7.37
600	1.17	700	3.27	800	7.02
600	1.19	700	3.30	800	7.15
600	1.21	700	3.17	800	7.20
600	1.23	700	3.22	800	7.10

The changes in the heat capacity ΔC_P for the equilibrium reactions were calculated from the values of C_P for H_2, H_2O, WO_3 /27/, W /78/, and for WO_2, according to Kopp's rule.

TABLE 57

Variation of the equilibrium constant $K_p = \frac{P_{H_2O}}{P_{H_2}}$ with temperature for the system $WO_{2.72} - H_2 - WO_2 - H_2O$

Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$
600	0.880	700	1.10	800	1.31	900	1.50
600	0.892	700	1.05	800	1.29	900	1.45
600	0.894	700	1.13	800	1.35	900	1.54
600	0.873	700	1.08	800	1.33	900	1.48
600	0.850	700	1.10	800	1.27	900	1.51
600	0.861	700	1.05	800	1.33	900	1.47

TABLE 58

Variation of the equilibrium constant $K_p = \frac{P_{H_2O}}{P_{H_2}}$ with temperature for the system $WO_2 - H_2 - W - H_2O$

Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$	Temperature, °C	$K_p = \frac{P_{H_2O}}{P_{H_2}}$
600	0.175	700	0.265	900	0.540
600	0.168	700	0.263	900	0.550
600	0.178	800	0.390	900	0.525
600	0.164	800	0.385	900	0.531
600	0.173	800	0.394	1000	0.687
600	0.171	800	0.401	1000	0.667
700	0.269	800	0.388	1000	0.690
700	0.272	800	0.386	1000	0.665
700	0.260	900	0.535	1000	0.670
700	0.267	900	0.521	1000	0.683

The data of Tables 55 — 58 were processed by the methods of Σ-functions and least squares. The values ΔF^0_{298} = 109,200 cal/mole and ΔH^0_{298} = 115,600 cal/mole for the reaction $2H_2 + O_2 = 2H_2O$ /27/ were used to calculate the functions ΔH^0_T and ΔF^0_T of each oxide. The values of S^0_{298} for W and O_2 /140/ were then used to calculate the standard entropies of these oxides. The results of these calculations are given below:

$$10WO_3 + H_2 \rightarrow 10WO_{2.90} + H_2O, \qquad (I)$$

$$\Delta H^\circ_T = 42,300 + 1.90T - 33.1 \cdot 10^{-3}T^2 + 0.04 \cdot 10^5 \cdot \frac{1}{T},$$

$$\Delta F^\circ_T = 42,300 - 1.90T \ln T + 33.1 \cdot 10^{-3}T^2 + \frac{0.02 \cdot 10^5}{T} - 66.0T,$$

$$\Delta H^\circ_{298} = +39.9 \pm 1.0 \text{ kcal}, \quad \Delta F^\circ_{298} = +22.4 \pm 1.0 \text{ kcal};$$

$$W + \frac{3}{2}O_2 \rightarrow WO_3,$$

$$\Delta H^\circ_{298} = -202.8 \pm 1.4 \text{ kcal/g} \cdot \text{atom},$$

$$S^\circ_{298}(WO_3) = 19.1 \pm 1.4 \text{ cal/g} \cdot \text{atom} \cdot W \cdot \text{deg}$$

$$\frac{100}{18}WO_{2.90} + H_2 \rightarrow \frac{100}{18}WO_{2.72} + H_2O, \qquad (II)$$

$$\Delta H_T^\circ = 19{,}100 - 3.35 \cdot T + 0.89 \times 10^{-3} T^2 + \frac{0.04 \cdot 10^5}{T},$$

$$\Delta F_T^\circ = 19{,}100 - 3.35T \ln T - 0.89 \times 10^{-3} T^2 + \frac{0.02 \cdot 10^5}{T} - 44.1T,$$

$$\Delta H_{298}^\circ = +18.2 \pm 1.0 \text{ kcal}, \quad \Delta F_{298}^\circ = +11.6 \pm 1.0 \text{ kcal};$$

$$W + \frac{2.90}{2}O_2 \rightarrow WO_{2.90},$$

$$\Delta H_{298}^\circ = -193.1 \pm 1.4 \text{ kcal/g} \cdot \text{atom},$$

$$S_{298}^\circ(WO_{2.90}) = 23.6 \pm 1.4 \text{ cal/g} \cdot \text{atom} \cdot W \cdot \text{deg}$$

$$\frac{100}{72}WO_{2.72} + H_2 \rightarrow \frac{100}{72}WO_2 + H_2O, \qquad (III)$$

$$\Delta H_T^\circ = 6110 - 3.35T + 0.89 \cdot 10^{-3} T^2 + \frac{0.04 \cdot 10^5}{T},$$

$$\Delta F_T^\circ = 6110 + 3.35T \ln T - 0{,}89 \times 10^{-3} T^2 + \frac{0.02 \cdot 10^5}{T} - 28.6T.$$

$$\Delta H_{298}^\circ = 5.2 \pm 1.0 \text{ kcal}, \quad \Delta F_{298}^\circ = 3.2 \pm 1.0 \text{ kcal};$$

$$W + \frac{2.72}{2}O_2 \rightarrow WO_{2.72},$$

$$\Delta H_{298}^\circ = -180.3 \pm 1.4 \text{ kcal/g} \cdot \text{atom},$$

$$S_{298}^\circ(WO_{2.72}) = 25.0 \pm 1.4 \text{ cal/g} \cdot \text{atom} \cdot W \cdot \text{deg}.$$

$$\frac{1}{2}WO_2 + H_2 \rightarrow \frac{1}{2}W + H_2O, \qquad (IV)$$

$$\Delta H_T^\circ = 10{,}125 - 3.48T + 1.08 \cdot 10^{-3} T^2 + \frac{0.04 \cdot 10^5}{T},$$

$$\Delta F_T^\circ = 10{,}125 + 3.48T \ln T - 1.08 \cdot 10^{-3} T^2 + \frac{0.02 \cdot 10^5}{T} - 30.7T,$$

$$\Delta H_{298}^\circ = 9.2 \pm 0.5 \text{ kcal}, \quad \Delta F_{298}^\circ = 6.8 \pm 0.5 \text{ kcal},$$

$$\Delta H_{298}^\circ = 134.0 \pm 0.7 \text{ kcal/g} \cdot \text{atom},$$

$$S_{298}^\circ(WO_2) = 19.7 \pm 1.0 \text{ cal/g} \cdot \text{atom} \cdot W \cdot \text{deg}.$$

Table 59 compares the heat of formation of tungsten oxides obtained by the equilibrium and calorimetric methods. The agreement shown is very good.

TABLE 59

Heats of formation of tungsten oxides

Oxide	ΔH°_{298}, kcal/g-atom	
	combustion	equilibrium
WO_3	-199 ± 1	202.8 ± 1.4
$WO_{2.90}$	-193 ± 1	193.1 ± 1.4
$WO_{2.72}$	-183 ± 1	-180.3 ± 1.4
WO_2	-137 ± 1	-134.0 ± 0.7

It should be noted that the data of Griffis /76/ are in good agreement with those of Vasil'eva, Gerasimov, and Simanov /95/, and the data of the Soviet authors are reported as being exceptionally accurate.

Morozova and Getskina /82/ ignited $WO_{2.67}$ together with benzoic acid in a high-precision vacuum calorimeter and found its heat of combustion as $\Delta H^{p}_{0_{comb.}} = 24.8 \pm 0.2$ kcal/g-formula. This value was used to calculate the heat of formation of $WO_{2.67}$, which is -175.5 ± 0.2 kcal/g. formula.

Reduction of tungsten carbide by hydrogen.

The reaction $W_5C_2 + 4H_2 = 5W + 2CH_4$ was studied by Schenk and coworkers /137/. Kelley /34/ used the data of these authors to derive the following equations for the heat content and the free energy:

$$\Delta H^{\circ}_{T} = 41,100 + 7T \text{ cal};$$

$$\Delta F^{\circ}_{T} = 41,100 - 16.1T \log T - 10.16T \text{ cal}.$$

The heat content and free energy for this reaction, calculated by the above equations, are, respectively:

$$\Delta H^{\circ}_{298} = 43,190 \text{ cal};$$

$$\Delta F^{\circ}_{298} = 26,200 \text{ cal}.$$

Reduction of tungsten sulfide by hydrogen.

Tungsten sulfide, when heated to 800° in a hydrogen atmosphere, is reduced to metallic tungsten, according to the reaction:

$$WS_2\,(s) + 2H_2 \rightleftharpoons W\,(s) + 2H_2S.$$

The equilibrium conditions of this reaction were studied by Parravano and Malquori /106/. These authors give the temperature variation of the equilibrium constant $K_p = \frac{P_{H_2S}}{P_{H_2}}$ as follows:

Temperature, °C	795	895	985	1065
$K_p = \frac{P_{H_2S}}{P_{H_2}}$	0.0140	0.0263	0.0420	0.0740

Chapter 2

THERMODYNAMIC PROPERTIES OF MOLYBDENUM AND OF ITS MORE IMPORTANT COMPOUNDS

7. METALLIC MOLYBDENUM (M = 95.95)

Crystalline structure, density, and melting point

Isotopes of molybdenum. There are seven isotopes of molybdenum /1/:

Mass number	92	94	95	96	97	98	100
Isotope content, %	15.84	9.04	15.72	16.53	9.46	23.70	9.63

Crystal structure of molybdenum. Structure type A2, space group O_h^9 with a = 3.1410 Å (Jette, Foote /2/, Owen, Iball /3/, Van Arkel /4/) or a = 3.139 Å (Hägg /5/).

Atomic volume and density of molybdenum. The atomic volume of molybdenum is 9.38 $cm^3/g \cdot atom$, according to Scott /6/, and 9.34 $cm^3/g \cdot atom$, according to Simon and Zeidler /7/.

The density of solid molybdenum, measured on samples of pressed powder, which were subjected to sintering and subsequent forging, is 10.02 g/cm^3. The same molybdenum in the form of wire of diameters of 3.75 and 0.25 mm has a density of 10.04 and 10.29 g/cm^3, respectively /8/. Molybdenum in crude form exhibits a density of 10.16 g/cm^3 /9/. Very pure molybdenum powder has a density of 10.281 g/cm^3 /9/. Hull /10/ and Davey /11/ determined the density of molybdenum by X-ray methods. The first author found a density of 10.16 g/cm^3, the second 10.21 ± 0.03 g/cm^3. Neuburger /12/ and Owen and Iball /3/ found 10.231 g/cm^3.

Thermal expansion of molybdenum. The coefficients of linear expansion α for intensely cold worked molybdenum wire are given below at different temperatures /13/:

Temperature, °C	25 — 100	500	1000	1500	2000
Coefficient of linear expansion $\alpha \cdot 10^6$ ...	4.9	5.1	5.5	6.2	7.2

Demarquay /13/ gives the following equations for the temperature dependence of α:
in the range 20 to 1300°

$$\alpha_t = 4.65 \cdot 10^{-6} + 0.9 \cdot 10^{-9} t,$$

and in the range 1300 to 2250°

$$\alpha_t = 6.8 \cdot 10^{-3} t^{-1} - 5.0 \cdot 10^{-6} + 4.4 \cdot 10^{-9} t.$$

Edwards and co-workers /14/ determined the thermal expansion of molybdenum in the temperature range 1100 to 2500°K and derived the following equation

$$\frac{\Delta a_0}{a} = 0.987 \cdot 10^{-3} + 2.4 \cdot 10^{-6} (T - 273) + 2.2 \cdot 10^{-9} (T - 273)^2.$$

Melting point of molybdenum. Table 60 contains values of the melting point of molybdenum as determined by various authors.

TABLE 60

Melting point of molybdenum

Melting point, °C	Method	Year	Author	Reference
2567 ± 40	Optical	1923	Pirani, Alterthum	/15/
2622 ± 40	"	1925	Worthing	/16/
2450	In nitrogen atmosphere	1948	Ol'shanskii	/17/

The most reliable values of the melting point of molybdenum as selected by various authors are presented in Table 61.

TABLE 61

Melting point of molybdenum
(proposed values)

Melting point, °K	Year	Author	Reference
2895	1927	Landolt-Bornstein	/18/
2840 – 2895	1939	Van Arkel	/28/
2895	1949	Stull	/20/
2883	1952	Rossini et al.	/21/
2873	1956	Kubaschewski, Evans	/22/
2890	1956	Stull, Sinke	/23/

We consider 2890°K as the best value for the melting point of molybdenum.

Vapor pressure and boiling point of molybdenum

Boiling point of molybdenum. Table 62 presents the experimental values, and Table 63 the most reliable values, of the boiling point of molybdenum.

TABLE 62

Boiling point of molybdenum determined from its vapor pressure curve

Boiling point, °C	Year	Author	Reference
3617	1914	Langmuir, Mackay	/24/
3560	1920	Van Liempt	/25/
5687	1927	Jones and co-workers	/26/

TABLE 63

Boiling point of molybdenum
(proposed values)

Boiling point, °K	Year	Author	Reference
5077	1935	Kelley	/27/
3833—5960	1939	Van Arkel	/28/
5550	1956	Kubaschewski, Evans	/22/
5100	1956	Stull, Sinke	/23/

We consider 5100°K to be the most reliable value.

Temperature of sublimation of molybdenum. It was experimentally determined by Zwikker /29/ that metallic molybdenum sublimes at 4507°.

Vapor pressure of molybdenum. The vapor pressure of molybdenum was first determined by Langmuir and Mackay /24/ from their experiments on the rate of vaporization of molybdenum wire. Results are given in Table 64.

TABLE 64

Vapor pressure of molybdenum /24/

Temperature, °K	Rate of vaporization, $g/cm^3 \cdot sec$	Vapor pressure, mm Hg
1800	$0.0863 \cdot 10^{-9}$	$6.43 \cdot 10^{-9}$
2000	$10.0000 \cdot 10^{-9}$	$789.00 \cdot 10^{-9}$
2200	$0.4800 \cdot 10^{-6}$	$39.60 \cdot 10^{-6}$
2400	$12.0000 \cdot 10^{-6}$	$1027.00 \cdot 10^{-6}$
2600	$1.7910 \cdot 10^{-4}$	$160.00 \cdot 10^{-4}$
2800	$18.1000 \cdot 10^{-4}$	$1679.00 \cdot 10^{-4}$

The vapor pressure of molybdenum from 1000°K to the boiling point, according to Jones, Langmuir, and Mackay /26/, is given in Table 65.

TABLE 65

Vapor pressure of molybdenum /26/

Temperature, °K	Rate of vaporization, $g/cm^3 \cdot sec$	Vapor pressure, bars	Temperature, °K	Rate of vaporization, $g/cm^3 \cdot sec$	Vapor pressure, bars
1000	$1.37 \cdot 10^{-24}$	$1.01 \cdot 10^{-19}$	3400	$5.60 \cdot 10^{-3}$	$7.70 \cdot 10^{2}$
1400	$1.29 \cdot 10^{-15}$	$1.13 \cdot 10^{-10}$	3800	$3.50 \cdot 10^{-2}$	$5.10 \cdot 10^{3}$
1800	$1.06 \cdot 10^{-10}$	$1.05 \cdot 10^{-6}$	4200	$1.50 \cdot 10^{-1}$	$2.30 \cdot 10^{4}$
2200	$1.30 \cdot 10^{-7}$	$1.43 \cdot 10^{-2}$	4800	$7.70 \cdot 10^{-1}$	$1.30 \cdot 10^{5}$
2600	$1.57 \cdot 10^{-5}$	1.87	5200	1.80	$3.00 \cdot 10^{5}$
3000	$5.00 \cdot 10^{-4}$	64.00	5900*	5.60	$1.00 \cdot 10^{6}$

* Boiling point

The vapor pressure of molybdenum from 1200 to 2500°K was also determined by Zwikker /29/ and his results are shown in Table 66.

TABLE 66

Vapor pressure of molybdenum /29/

Temperature, °K	Rate of vaporization, g/cm3·sec.	Vapor pressure, mm Hg	Temperature, °K	Rate of vaporization, g/cm3·sec.	Vapor pressure, mm Hg
1200	$1.23 \cdot 10^{-20}$	$7.47 \cdot 10^{-19}$	2000	$2.07 \cdot 10^{-9}$	$1.62 \cdot 10^{-7}$
1400	$1.20 \cdot 10^{-16}$	$7.88 \cdot 10^{-15}$	2200	$7.30 \cdot 10^{-8}$	$6.07 \cdot 10^{-6}$
1600	$1.23 \cdot 10^{-13}$	$8.63 \cdot 10^{-12}$	2400	$1.40 \cdot 10^{-6}$	$1.20 \cdot 10^{-4}$
1800	$2.82 \cdot 10^{-11}$	$2.10 \cdot 10^{-9}$	2500	$5.03 \cdot 10^{-6}$	$4.41 \cdot 10^{-4}$

Langmuir and Mackay /24/ give the following equations for the rate of vaporization and the vapor pressure as functions of temperature:

$$\log m = 17.11 - \frac{38,600}{T} - 1.76 \log T,$$

$$\log P = 17.11 - \frac{38,600}{T} - 1.26 \log T \text{ mm Hg}.$$

On the basis of the experimental results of the above authors, Van Liempt /25/ derived the following equation for the vapor pressure as a function of temperature. For his equation Van Liempt /25/ used a boiling point of 3833°K:

$$\pi = -\frac{37,040}{T} + 9.67,$$

where π is Briggs' logarithm of the vapor pressure in atm.

Van Arkel /28/ gives the following equation for the vapor pressure of solid molybdenum from 2000 to 2900°:

$$\log P = -\frac{34,000}{T} + 0.045 \log T - 0.000271 T + 10.88;$$

According to the same author /28/, the vapor pressure of liquid molybdenum from 2900 to 3500° is expressed by the following equation:

$$\log P = -\frac{32,150}{T} + 0.045 \log T - 0.000271 T + 10.24.$$

Edwards and co-workers /30/ determined the vapor pressure of molybdenum by vacuum vaporization and from their results obtained the following equation, valid from 2151 to 2462°K:

$$R \ln P = -\frac{155,550}{T} - 3.452 \cdot 10^{-3} T + 41.60.$$

The accuracy of the measurements was: temperature ±3.4°, time ±5 sec, losses in weight ±0.0001 g, surface ±0.0025 cm^2.

Kubaschewski and Evans /22/, with reference to the work of Edwards et al. /30/, propose the following equation for the vapor pressure of solid molybdenum, valid between 2980°K and the melting point:

$$\log P(\text{mm Hg}) = -\frac{31,060}{T} - 0.2 \log T + 9.41$$

Kelley /27/ gives the following values for the vapor pressures of liquid molybdenum:

Temperature, °K	3000	3330	3750	4300	4580	4810	5077
Pressure, mm Hg	0.076	0.76	7.6	76	190	380	760

Table 67 gives the vapor pressure of liquid molybdenum, according to Stull /20/.

TABLE 67

Vapor pressure of liquid molybdenum according to Stull /20/

Temperature, °C	Vapor pressure, mm Hg	Temperature, °C	Vapor pressure mm Hg
3375	1	4237	60
3666	5	4382	100
3808	10	4595	200
3963	20	4826	400
4132	40	5077	760

Figure 1 shows graphically the function $\log P = f\frac{1}{T}$ for liquid molybdenum plotted according to the values of Kelley /27/ and Stull /20/. It can be seen from this figure that the points of Stull /20/ fit a straight line better than those of Kelley /27/. Therefore, we consider the data of Stull /20/, which seem to be average values of data compiled by various authors, the most reliable for thermodynamic calculations.

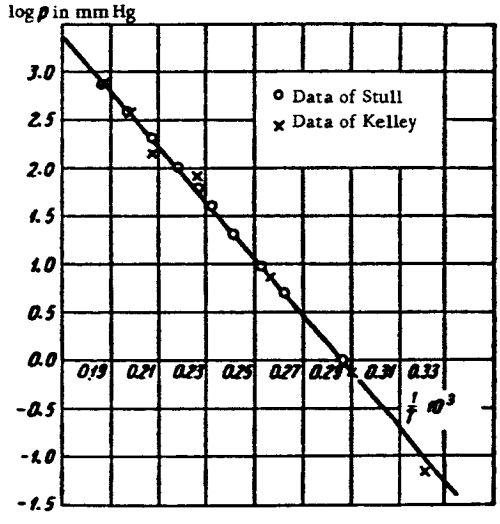

FIGURE 1. Vapor pressure of molybdenum.

Heat capacity, heat capacity change during vaporization and sublimation, heat, entropy, and free energy of vaporization, fusion, boiling, and sublimation

Heat capacity of molybdenum. Tables 68 and 69 show the specific and atomic heat capacities of molybdenum according to various authors.

TABLE 68

Average specific heat capacity of molybdenum

Temperature, °C	Specific heat capacity cal/g · degrees	Author	Reference
20 — 77	0.0141	Dewar	/31/
85 — 253	0.0555	Richards, Jackson	/32/
288 — 364	0.0723	Defacqz, Guichard	/33/
288 — 537	0.0735		
288 — 713	0.0740		
293 — 373	0.0647	Stücker	/34/
293 — 823	0.0722		
273 — 373	0.06054	Stern	/35/
273 — 714.5	0.06333		
373 — 1773	0.06227 — 0.0781	Wust, Meuthen, Durrer	/36/
233	0.0564	Cooper, Langstrath	/38/
248	0.0071		
273	0.0589		

TABLE 69

True atomic heat capacity of molybdenum

Temperature, °C	Atomic heat capacity cal/g · at · deg	Author	Reference	Temperature, °C	Atomic heat capacity cal/g · at · deg	Author	Reference
10	0.010	Kelley	/37/	150	4.49	Kelley	/37/
15.97	0.040	Simon, Zeidler	/7/	200	5.10	Kelley	/37/
17.97	0.044			200.2	5.09	Simon, Zeidler	/7/
20.66	0.073			274.7	5.53		
25	0.13	Kelley	/37/	298.1	5.61	Kelley	/37/
27.54	0.172	Simon, Zeidler	/7/	298	5.61	Rossini et al	/21/
31.52	0.264			298	5.68	Stull, Sinke	/23/
34.04	0.331			300	5.69		
38.10	0.459			400	5.97		
50	0.94	Kelley	/37/	500	6.15		
56.00	1.230	Simon, Zeidler	/7/	600	6.28		
64.3	1.640			700	6.35		
69.5	1.900			800	6.44		
91.6	2.88			900	6.55		
100	3.19	Kelley	/37/	1000	6.70		
105.6	3.38	Simon, Zeidler	/7/	1100	6.86		
112.8	3.63			1200	7.05		
120.4	3.84			1300	7.24		
144.6	4.38			1400	7.45		

TABLE 69 (continued)

Temperature, °C	Atomic heat capacity cal/g·at·deg	Author	Reference	Temperature, °C	Atomic heat capacity cal/g·at·deg	Author	Reference
1500	7.65	Stull, Sinke	/23/	2300	9.02	Stull, Sinke	/23/
1600	7.83			2400	9.19		
1700	8.00			2500	9.36		
1800	8.18			2600	9.53		
1900	8.35			2700	9.70		
2000	8.52			2800	9.87		
2100	8.69			2900	10.00		
2200	8.85			3000	10.00		

The heat capacity of gaseous molybdenum, according to the results of Stull and Sinke /23/, is given in Table 70.

TABLE 70

Heat capacity of [gaseous] molybdenum according to Stull and Sinke /23/

Temperature, °K	Atomic heat capacity cal/g·deg	Temperature, °K	Atomic heat capacity cal/g·deg	Temperature, °K	Atomic heat capacity cal/g·deg
298	4.9680*	1100	4.97	2100	5.18
298	4.97	1200	4.97	2200	5.25
300	4.97	1300	4.97	2300	5.34
400	4.97	1400	4.98	2400	5.44
500	4.97	1500	4.98	2500	5.56
600	4.97	1600	5.00	2600	5.69
700	4.97	1700	5.02	2700	5.84
800	4.97	1800	5.04	2800	6.00
900	4.97	1900	5.08	2900	6.19
1000	4.97	2000	5.13	3000	6.39

* According to Rossini et al. /21/.

Table 71 presents equations giving the variation of specific and atomic heat capacities of molybdenum with temperature, according to various authors.

Heat of fusion of molybdenum. L_{fus} = 1000 to 5000 cal/g·atom /25/, L_{fus} = 6600 cal/g·atom /27/, L_{fus} = 6.6 ± 0.7 kcal/g·atom /22/, L_{fus} = 6.6 kcal/g·atom /23/.

Entropy of fusion of molybdenum. According to Kelley /27/, the entropy of fusion of molybdenum is ΔS°_{fus} = 2.3 e.u.

Heat capacity change during vaporization of molybdenum. The heat capacity change during the vaporization of molybdenum is ΔC_P = −5 cal/deg·g·atom /27/.

TABLE 71

Equations for the variation of specific and atomic heat capacities of molybdenum with temperature

Equation	Temperature range	Author	Reference
$C_p = 4.88 + 2.48 \cdot 10^{-3} \cdot T$	—	Jones et al.	/26/
$C_v = 85 \cdot 10^{-7} \cdot T^3$	16 — 34°K	Cooper, Langstrath	/38/
$c_p = 0.05973 + 16.19 \cdot 10^{-6} \cdot t$	0 — 444.5°C	Stern	/35/
$c_p = 0.06069 + 1.2 \cdot 10^{-5} \cdot T - \frac{361}{T}$	0 — 500°C	Bronson et al	/39/
$c_p = 0.0593 + 1.3 \cdot 10^{-5}(T+40) - \frac{8.0265}{(T+40)^{1.06}}$	From -40 to 250°C	Cooper, Langstrath	/38/
* $C_p = 5.48 + 1.30 \cdot 10^{-3} \cdot T$	298—1800°K	Kelley	/40/
$C_p(\tau) = 5.69 + 1.88 \cdot 10^{-3} \cdot T - 0.503 \cdot 10^5 T^{-2}$	To 1773°K	Kelley	/27/
$C_p(g) = 4.97$			

* Accuracy of this equation 1%.

Heat of vaporization of molybdenum. The values of the heat of vaporization of molybdenum are shown in Table 72.

TABLE 72

Heat of vaporization of molybdenum

Temperature, °K	Heat of vaporization cal/g · atom	Author	Reference
0	177000	Langmuir, Mackay	/24/
0	154000	Zwikker	/29/
0	146000	Jones et al.	/26/
0	170400	Simon, Zeidler	/7/
0	155550	Edwards et al.	/30/
0	142000	Stull, Sinke	/23/
B. p.	169600	Liempt	/25/
298.1	152310	Kelley	/27/
5077	128415		
5550	121.0 ± 9.0 kcal/g · atom	Kubaschewski, Evans	/22/

Entropy of vaporization of molybdenum. At 5077°K, $\Delta S_{vap} = 25.3$ cal/g · atom · degree /27/.

Free energy of vaporization of molybdenum. Kelley /27/ gives for this function the following equation:

$$\Delta F^0_{T_{vap}} = 153{,}800 + 11.5 T \log T - 72.91 T,$$

hence, $\Delta F^0_{298} = 140{,}549$ cal/g · atom.

Heat capacity change during sublimation of molybdenum. The change in the heat capacity at sublimation of molybdenum is expressed by the equation $\Delta C_p = -0.72 - 1.88 \cdot 10^{-3} T + 0.503 \times 10^5 T^{-2}$ cal/g·atom·deg. /27/.

Heat of sublimation of molybdenum. The heats of sublimation of molybdenum in the range 298 to 3000°K are given in Table 73 /23/.

TABLE 73

Heat of sublimation of molybdenum /23/

Temperature, °C	Heat of sublimation cal/g · atom	Temperature, °C	Heat of sublimation cal/g · atom	Temperature, °C	Heat of sublimation cal/g · atom
298	155500*	1100	156394	2100	153607
298	157500	1200	156191	2200	153259
300	157498	1300	155968	2300	152879
400	157411	1400	155725	2400	152518
500	157300	1500	155473	2500	152137
600	157175	1600	155192	2600	151749
700	157036	1700	154903	2700	151366
800	156893	1800	154596	2800	150978
900	156740	1900	154282	2900	143997**
1000	156577	2000	153952	3000	143626**

* From Rossini et al /21/

** Heat of vaporization.

The heat of sublimation, L_{subl}, of molybdenum at its melting point, is 134.5 ± 7.0 kcal/g·atom./22/.

The variation of the heat of sublimation with temperature may be represented by the following equation, according to Kelley /27/:

$$L_{subl} = 155,960 - 0.72T - 0.94 \cdot 10^{-3}T^2 - 0.503 \cdot 10^5 T^{-2},$$

hence,

$$L_{298}^{subl} = 155,493 \text{ cal/g} \cdot \text{atom}.$$

Free energy of sublimation of molybdenum. Stull and Sinke /23/ calculated the free energy of sublimation of molybdenum in the range 298 to 3000°K. The calculated values for ΔF_{subl} are given in Table 74. This table contains also the corresponding $\log K_p$'s for the sublimation process.

TABLE 74

Free energy of sublimation of molybdenum and $\log K_p$'s for the sublimation process

T, °K	L_{subl} cal/g · at.	$-\log K_p$	T, °K	L_{subl} cal/g · at.	$-\log K_p$	T, °K	L_{subl} cal/g · at.	$-\log K_p$
298	144200	—	1100	117905	23.427	2100	83503	8.721
298	146578	107.449	1200	114419	20.840	2200	80505	7.997
300	146509	106.740	1300	110936	18.651	2300	77163	7.332
400	142859	78.061	1400	107467	16.777	2400	73894	6.728
500	139230	60.861	1500	104053	15.161	2500	70637	6.175
600	135629	49.406	1600	100632	13.745	2600	67379	5.663
700	132046	41.230	1700	97222	12.498	2700	64129	5.190
800	128477	35.101	1800	93846	11.393	2800	60930	4.755
900	124943	30.342	1900	90480	10.407	2900	61260*	4.616*
1000	121427	26.540	2000	87132	9.520	3000	58426*	4.256*

* These numbers relate to the vaporization of liquid molybdenum.

The variation of the free energy of sublimation of molybdenum with temperature can be expressed by the following equation:

$$\Delta F^{\circ}_{subl} = 155{,}960 - 1.66T\log T + 0.94\cdot 10^{-3}T^2 - 0.2515\cdot 10^{5}T^{-1} - 42.31\cdot T,$$

hence, $\Delta F^{0}_{298} = 144{,}570$ cal/g · atom /27/.

Heat content, entropy, and free energy function of molybdenum

Heat content of molybdenum. The values of the heat content of solid molybdenum are presented in Table 75.

The values of this table fit the following equation, valid from 298 to 1800°K:

$$H_T - H_{298} = 5.48T + 0.65\cdot 10^{-3}T^2 - 1692 \text{ cal/g·atom.}$$

The accuracy of this equation is 0.5%.

TABLE 75

Heat contents of solid molybdenum

T, °K	$H_T - H_{298}$ cal/g · atom	T, °K	$H_T - H_{298}$ cal/g · atom	T, °K	$H_T - H_{298}$ cal/g · atom
400	610	900	3765	1400	7250
500	1215	1000	4440	1500	7985
600	1830	1100	5125	1600	8740
700	2460	1200	5825	1700	9510
800	3150	1300	6530	1800	10300

The heat content of solid and gaseous molybdenum, according to Stull and Sinke /23/, is given in Table 76. (The second column of this table refers to solid molybdenum, the third to gaseous molybdenum.)

TABLE 76

Heat content of solid and gaseous molybdenum

T, °K	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.	T, °K	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.	T, °K	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.	$H^{\circ}_T - H^{\circ}_{298}$ cal/g · at.
298	0	0	1200	5790	4481	2200	13770	9529
300	11	9	1300	6510	4978	2300	14680	10059
400	595	506	1400	7250	5475	2400	15580	10598
500	1203	1003	1500	8000	5973	2500	16510	11147
600	1825	1500	1600	8780	6472	2600	17460	11709
700	2460	1996	1700	9570	6973	2700	18420	12286
800	3100	2493	1800	10380	7476	2800	19400	12878
900	3750	2990	1900	12000	7982	2900	26990*	13487
1000	4410	3487	2000	12040	8492	3000	27990*	14116
1100	5090	3984	2100	12900	9007			

* For liquid molybdenum.

Entropy of molybdenum. The entropy of solid molybdenum, as determined by various authors, is given in Table 77.

TABLE 77

Entropy of solid molybdenum
(Proposed values)

Entropy cal/deg·g-atom	Year	Author	Reference
6.83	1932	Kelley	/41/
6.83	1930	Ulich	/42/
6.83 ± 0.5	1950	Kelley	/37/
6.83 ± 0.1	1956	Kubaschewski, Evans	/22/
6.83	1952	Rossini et al	/21/
6.83	1956	Stull, Sinke	/23/

According to Kelley /37/, the entropy of gaseous molybdenum is S^0_{298} = 43.47 ± 0.01 cal/deg·g·atom. Rossini and co-workers /21/ give the value S^0_{298} = 43.462 cal/deg·g·atom.

The entropy change of solid molybdenum in the range 400 to 1800°K is given in Table 78, according to Kelley /40/.

TABLE 78

Entropy of solid molybdenum /40/

T, °K	$S^\circ_T - S^\circ_{298}$ cal/deg·g·atom	T, °K	$S^\circ_T - S^\circ_{298}$ cal/deg·g·atom	T, °K	$S^\circ_T - S^\circ_{298}$ cal/deg·g·atom
400	1.76	900	6.85	1400	9.91
500	3.12	1000	7.56	1500	10.42
600	4.24	1100	8.21	1600	10.91
700	5.21	1200	8.82	1700	11.38
800	6.07	1300	9.38	1800	11.83

Free energy function. Stull and Sinke /23/ give entropies and free energy functions $\Phi'' = -\frac{F^\circ - H^0_{298}}{T}$ for solid and gaseous molybdenum in the temperature range 298 to 3000°K. These values are presented in Table 79.

TABLE 79

Entropy and free energy function of molybdenum /23/

T, °K	S°_s cal/deg·g·atom	S°_g cal/deg·g·atom	Φ°_s cal/deg·g·atom	Φ°_g cal/deg·g·atom
298	6.83	43.46	6.83	43.46
300	6.86	43.49	6.83	43.46
400	8.54	44.92	7.06	43.66
500	9.89	46.03	7.49	44.03
600	11.03	46.94	7.99	44.44
700	12.00	47.70	8.49	44.85

TABLE 79 (continued)

T, °K	S°_{s} cal/deg·g·atom	S°_{g} cal/deg·g·atom	Φ''_{s} cal/deg·g·atom	Φ''_{g} cal/deg·g·atom
800	12.85	48.37	8.98	45.26
900	13.62	48.92	9.46	45.63
1000	14.32	49.47	9.91	45.99
1100	14.96	49.95	10.34	46.33
1200	15.57	50.38	10.75	46.65
1300	16.14	50.78	11.14	46.96
1400	16.68	51.15	11.51	47.24
1500	17.21	51.49	11.88	47.51
1600	17.71	51.81	12.23	47.77
1700	18.19	52.12	12.57	48.02
1800	18.65	52.40	12.89	48.25
1900	19.10	52.68	13.21	48.48
2000	19.53	52.94	13.51	48.70
2100	19.95	53.19	13.81	48.91
2200	20.36	53.43	14.11	49.10
2300	20.75	53.67	14.37	49.30
2400	21.14	53.90	14.65	49.49
2500	21.52	54.12	19.92	49.67
2600	21.89	54.34	15.18	49.84
2700	22.25	54.56	15.43	50.01
2800	22.61	54.77	15.69	50.18
2900	26.46*	54.99	17.16*	50.34
3000	26.80*	55.20	17.47*	50.50

* The two last values refer to the entropy and free energy function of liquid molybdenum.

8. MOLYBDENUM OXIDES

The following oxides of molybdenum exist: MoO_3 — α-oxide; $MoO_{2.889}$ or Mo_9O_{26} — β'-oxide; $MoO_{2.875}$ or Mo_8O_{28} — β-oxide; $MoO_{2.75}$ or Mo_4O_{11} — γ-oxide and MoO_2-δ-oxide. These data are taken from Magneli, as quoted by Hegedüs and co-workers./43/.

Molybdenum dioxide MoO_2 (M = 127.95)

Crystal structure of MoO_2. Molybdenum dioxide has a distorted rutile structure (Brewer /44/). The lattice parameters are a = 5.61 Å, b = 4.84 Å, c = 5.53 Å, and α = 119.6° (Magneli /45/).

Molar volume and density of MoO_2. The molar volume of MoO_2 is 20 cm^3/mole (Biltz /46/).

According to Stefanovics /47/, the density of MoO_2 is 6.342 g/cm^3 at 14°.

Temperature of disproportionation of MoO_2. According to Brewer /44/, solid molybdenum dioxide disproportionates into solid molybdenum and gaseous oxygen at 2250 ± 50°K and at a pressure of 1 atm.

Vapor pressure of MoO_2. Blackburn and co-workers /48/ measured the vapor pressure of molybdenum oxides by the Knudsen effusion method. They found that some of the solid MoO_2 sublimes without decomposition, while the greater part disproportionates into gaseous MoO_3 and solid molybdenum.

Heat of disproportionation of MoO_2. According to Blackburn et al. /48/, disproportionation of solid MoO_2 into gaseous MoO_3 and solid molybdenum is accompanied by the heat change ΔH^0_0 = 133.6 kcal/mole of MoO_3.

Energy of dissociation of MoO_2. Blackburn and co-workers report /48/ that the energy of dissociation, D_0^0, of gaseous MoO_2 into gaseous atomic molybdenum and oxygen is 284.6 kcal/mole at 0°K.

Entropy of MoO_2. King /49/ determined the heat capacity of MoO_2 in the range 51 to 298°K and from his results calculated the standard entropy of this compound, i.e., $S_{298}^0 = 11.06 \pm 0.05$ cal/deg·mole. According to Tonosaki /50/, the standard entropy of MoO_2 is 19.3 cal/deg·mole.

Kubaschewski and Evans /22/ give the standard entropy of MoO_2 as $S_{298}^0 = 13.6 \pm 2.0$ cal/deg·mole. The great discrepancies in the values of the absolute entropy of MoO_2 are evidently due to the difficulty of determining the heat capacity of this compound, which is unstable on heating.

Heat of formation of MoO_2. Tonosaki /50/ found the heat of formation ΔH_{298}^0 of solid MoO_2 to be −131.692 kcal/mole. The heat of formation of MoO_2 as determined by various authors has the following values:

$\Delta H_{298}^0 = -140.9$ kcal/mole (Stasliewicz et al. /51/);

$\Delta H_{298}^0 = -142.8$ kcal/mole (Mixter /52/);

$\Delta H_{298}^0 = -140.8$ kcal/mole (Mah /53/);

$\Delta H_{298}^0 = -131.0 \pm 2$ kcal/mole (Brewer /44/)

$\Delta H_{298}^0 = -139.5 \pm 3.0$ kcal/mole (Kubaschewski, Evans /22/);

$\Delta H_{298}^0 = -130$ kcal/mole (Rossini et al. /21/).

We consider Mah's value, $\Delta H_{298}^0 = -140.8$ kcal/mole /53/, the most reliable.

Entropy of formation of MoO_2. Tonosaki /50/ determined the entropy of formation of MoO_2 as $\Delta S_{298}^0 = -36.5$ cal/deg·mole. Brewer /44/ gives the value $\Delta S_{298}^0 = -36.6$ cal/deg·mole.

Free energy of formation of MoO_2. The value of the free energy of formation of MoO_2, according to /44/, is $\Delta F_{298}^0 = -120$ kcal/mole and, according to /50/, $\Delta F_{298}^0 = -120.816$ kcal/mole.

The variation of the free energy of formation of MoO_2 with temperature according to the reaction $Mo(s) + O_2 = MoO_2(s)$ is expressed by the following equation $\Delta F_T = 140,100 + 4.6T \log T - 55.8T$ cal, which is valid in the temperature range 298 to 1300°K. The accuracy of the equation is ±6 kcal /22/.

Molybdenum trioxide MoO_3 ($M = 143.95$)

Crystal structure of MoO_3. Structure type $D0_8$. Spatial group D_{2h}^{16}. Lattice parameters of the orthorhombic structure: $a = 3.9$ Å, $b = 13.8$ Å; $c = 3.7$ Å /53, 54/.

Molar volume and density of MoO_3. According to Hülsmann and Biltz /55/, the molar volume of MoO_3 is 30.69 at 21°; 30.47 at −78°; and 30.29 cm^3/mole at −195°.

The density values of MoO_3 are presented in Table 80.

Melting point of MoO_3. The melting point of molybdenum trioxide is presented in Table 81 according to various authors.

Stull /20/, Brewer /44/, and Kubaschewski and Evans /22/, consider 795° the best value for the melting point of MoO_3.

TABLE 80

Density of MoO_3

Temperature, °C	Density g/cm³	Year	Author	Reference
26	4.696	1915	Müller	/9/
19.5	4.500	1915	Wedekind, Horst	/56/
21	4.692	1934	Hülsmann, Biltz	/55/
-78	4.726			
-195	4.754			

TABLE 81

Melting point of MoO_3

Melting point, °C	Year	Author	Reference
791	1908	Groschuff	/57/
795	1921	Jaeger, Germs	/58/
795	1931	Feiser	/59/
795.2	1953	Cosgrove, Snyder	/60/

Boiling point of MoO_3. The boiling point of MoO_3, as determined by Feiser /59/, is 1155°. Kelley /27/ gives the value 1424°K, Kubaschewski and Evans /22/ 1553°K, Brewer /44/ 1530 ± 50°K at a pressure of 1 atm. and Rossini et al. /21/ 1428°K.

Vapor pressure of MoO_3. The vapor pressure of MoO_3 was determined by Feiser /59/. It was calculated on the assumption that losses in weight during vaporization of MoO_3 in a current of gas are proportional to the vapor pressure. The results of the investigation are given in columns 2 and 5 of Table 82. Columns 3 and 6 of the same table give the vapor pressure of MoO_3 as calculated by Ramsay-Young's rule for temperatures exceeding the melting point of MoO_3.

TABLE 82

Vapor pressure of MoO_3

Temperature, °K	Vapor pressure, mm Hg		Temperature, °K	Vapor pressure, mm Hg	
1	2	3	4	5	6
873	0.000	—	1123	23.4	17.9
883	0.009	—	1173	53.9	38.6
898	0.018	—	1223	105.1	77.2
923	0.050	—	1273	179.8	146.0
973	0.300	—	1323	288.3	261.2
993	0.600	—	1373	476.2	443.9
1023	1.750	—	1428	760.0	760.0
1073	10.100	7.7			

The discrepancy between the data of columns 2 and 5, 3 and 6 of Table 82 may be due, according to Feiser, to the possibility of polymerization of MoO_3 molecules.

Kelley /27/ used the data of columns 3 and 6 of Table 82 to derive the following equation for the variation of the vapor pressure of solid MoO_3 with temperature:

$$\log P(\text{atm}) = -\frac{15,110}{T} + 1.46 \log T - 1.32 \cdot 10^{-3} T + 9.071$$

and over liquid MoO_3

$$\log P(\text{atm}) = -\frac{11,820}{T} - 7.04 \log T + 30.494.$$

According to Kelley's /27/ equations, MoO_3 has the following values of vapor pressure.

Temperature, °K	934	999	1074(s)	1207(l)	1283	1350	1424
Vapor pressure, mm Hg	0.076	0.76	7.6	76	190	380	760

Stull /20/ compared the experimental results of various authors and gave the following values for the vapor pressure of solid and liquid MoO_3:

Temperature, °K	973*	1007	1058	1087	1124	1165	1190	1128	1287	1355	1424
Vapor pressure, mm Hg	0.3	1	5	10	20	40	60	100	200	400	760

Ueno /61/ studied the vapor pressure of MoO_3 in the range 635 to 675°, using a Knudsen effusion cell, and derived the following equation for the variation of the vapor pressure of solid MoO_3 with temperature:

$$\log P(\text{mm Hg}) = -\frac{13,902.7}{T} + 13.033.$$

Kubaschewski and Evans /22/ quote Ueno's equation /61/ for the vapor pressure of solid MoO_3, but consider the following equation more reliable:

$$\log P(\text{mm Hg}) = -\frac{16,150}{T} - 5.53 \log T + 32.08.$$

This equation is valid from 298° to the melting point. For liquid molybdenum the same authors give the equation

$$\log P(\text{mm Hg}) = -14,110 \cdot T^{-1} - 7.08 \log T + 34.54,$$

valid from the melting point to the boiling point.

Zelikman and co-workers /62/ measured the vapor pressure of MoO_3 by the effusion method and also by observing the boiling point at given pressures. By comparing the results of both methods, they concluded that MoO_3 polymerizes in the gaseous phase and found that from 950 to 1000° the composition of gaseous MoO_3 corresponds to $(MoO_3)_3$ or Mo_3O_9. The equation

$$\log P(\text{mm Hg}) = -\frac{7685}{T} + 8.26$$

was derived from vapor pressure curves presented below /62/. These curves were obtained by measurement of the boiling point of MoO_3 at fixed pressures.

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* Data of Rossini et al. /21/.

Temperature, °C	Pressure, mm Hg
905	53
960	100
1015	200
1057	300
1100	450
1155*	650

Blackburn and co-workers /48/ measured the vapor pressure with a Knudsen effusion cell and confirmed the fact that MoO_3 vaporizes as $(MoO_3)_3$.

Figure 2 shows the graph of the function $\log P$ f $\frac{1}{T}$ for gaseous MoO_3. It was plotted from the data of Stull /20/, Kelley /27/, Kubaschewski and Evans /22/, and Zelikman et al. /62/. Whereas the points of Stull /20/, Kelley /27/, and Zelikman et al. /62/ fit well into the plotted curve, those of Kubaschewski and Evans /22/ are located outside the curve. The high accuracy of the comparatively recent results of Zelikman et al. /62/ (1956) is indicated by the fact that they show good agreement with those of Stull /20/ and Kelley /27/. The best values for thermodynamic calculations are therefore considered to be those of Stull /20/, Kelley /27/, and Zelikman and co-workers /62/.

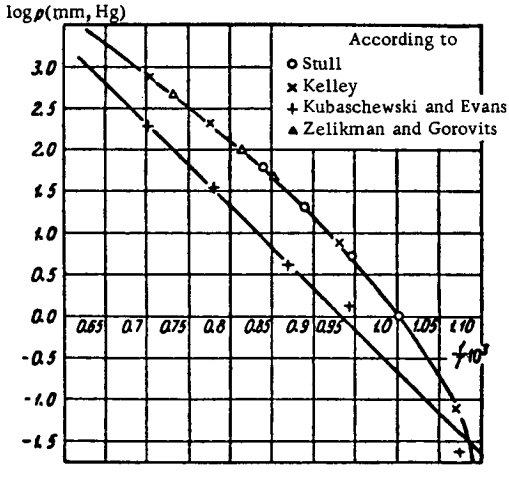

FIGURE 2. Vapor pressure of MoO_3.

Heat capacity of MoO_3. The heat capacity of solid MoO_3 at low temperatures shows the following variation with temperature:

Temperature, °K	10	25	50	100	150	200	289.1
Heat capacity, cal/mole	(0.06)	(0.08)	(3.16)	7.31	11.04	13.79	17.57

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* Extrapolation.

From the results of Seltz and co-workers /64/, Kelley /63/ derived the following equation, valid from 298 to 1068°K, for the variation of the molar heat capacity of solid molybdenum trioxide:

$$C_p = 13.6 + 13.5 \cdot 10^{-3} T.$$

Smith and co-workers /65/ note that the results of Seltz /64/ for the heat capacity of MoO_3 at temperatures below zero degree centigrade are not accurate enough to verify the function $C_P = f(T^2)$ in the range 0 to 60°K. For this reason, Smith and co-workers /65/ made a new investigation of the heat capacities of MoO_3 at low temperatures. The authors /65/ obtained their data by using the low-temperature calorimeter described in /66, 67/. The general accuracy of the determination of C_P was approximately 0.2% at temperatures higher than 50°K, and possibly 0.5% at 20°K.

TABLE 83

Experimental data on the heat capacity of solid MoO_3 /63/

T, °K	C_P cal/mole · deg	T, °K	C_P cal/mole · deg	T, °K	C_P cal/mole · deg
94.01	7.017	223.30	15.224	88.54	6.527
98.19	7.388	228.21	15.391	92.96	6.945
102.18	7.754	233.06	15.583	97.17	7.299
106.02	8.088	237.86	15.788	101.19	7.675
109.73	8.401	242.62	15.967		
113.31	8.698			19.16	0.367
116.79	8.970	241.77	15.948	24.65	0.578
121.10	9.312	246.45	16.120	24.47	0.735
126.20	9.716	251.10	16.295	29.89	0.949
131.10	10.085	255.70	16.458	31.86	1.066
135.85	10.447	260.27	16.611	35.64	1.301
140.49	10.762	264.79	16.676	40.69	1.730
145.03	11.076	269.28	16.951	44.48	2.100
149.46	11.368	273.74	17.094	47.72	2.425
153.79	11.640	278.15	17.275	50.56	2.707
158.04	11.918	282.54	17.384	54.53	3.097
162.22	12.165	286.89	17.544	59.43	3.606
167.21	12.449	291.20	17.704		
172.98	12.785	295.49	17.832	18.27	0.316
178.65	13.083	299.76	17.920	20.86	0.516
				23.68	0.580
176.10	12.964	55.25	3.173	30.02	0.890
181.69	13.264	58.72	3.524	36.99	1.418
187.18	13.541	63.10	3.995	41.58	1.827
192.58	13.826	67.02	4.390	45.24	2.188
197.89	14.076	70.62	4.754	48.36	2.492
203.13	14.308	73.97	5.074	51.12	2.759
208.28	14.577	77.12	5.397	55.02	3.143
213.38	14.778	80.11	5.703		
218.34	15.007	83.83	6.069		

Experimental data on C_P per mole of MoO_3 are presented in Table 83. They were obtained in the same order as given in Table 83.

The gaps inbetween the series of numbers separate data obtained in the further series of experiments.

Values of the heat capacities of solid MoO_3 in the range from 10 to 300°K at intervals of 10° are presented in Table 84.

According to Orr /68/ the heat capacity of solid molybdenum trioxide fits the following equation in the temperature range 298 to 1808°K: $C_p = 20.07 + 5.80 \cdot 10^{-3} T - 3.68 \cdot 10^{-5} T^2$. The accuracy of this equation is 2%.

TABLE 84

Heat capacities of MoO_3

T, °K	C_p cal/mole · deg	T, °K	C_p cal/mole · deg	T, °K	C_p cal/mole · deg
10	—	120	9.23	230	15.48
20	0.39	130	10.00	240	15.87
30	0.90	140	10.73	250	16.25
40	1.67	150	11.40	260	16.61
50	2.65	160	12.02	270	16.96
60	3.66	170	12.61	273.15	17.07
70	4.69	180	13.17	280	17.30
80	5.68	190	13.69	290	17.65
90	6.66	200	14.18	298.15	17.93
100	7,56	210	14.64	300	17.98
110	8.42	220	15.07		

Data on the molar heat capacity of liquid MoO_3 are given by Cosgrove and Snyder /60/.

Heat of fusion of MoO_3. The first measurements of the heat of fusion of MoO_3 were presented by Hoermann /69/ and Groschuff /70/. Kelley /71/ gives the average of these data, i.e., L_{fus} = 2500 cal. This value, however, is very low. Cosgrove and Snyder /60/ found by experiment that the heat of fusion L_{fus} of MoO_3 is 12,540 cal/mole. Kubaschewski and Evans /22/ consider the value 12.55 ± 0.40 kcal/mole to be the most reliable.

Heat of vaporization of MoO_3. The heat of vaporization of MoO_3, according to /62/, is 35.1 kcal/mole.

At its boiling point (1280°), the heat of vaporization L_{vap} of molybdenum trioxide is 42.7 ± 4.0 kcal/mole /22/.

Heat of sublimation of MoO_3. The experiments of Ueno /61/ showed that at 928.1°K, L_{subl} = 63.7 kcal/mole and at 298.1°K L_{subl} = 49.8 kcal/mole. Kubaschewski and Evans /22/ give the values 70.6 ± 5.0 kcal/mole and 62.2 ± 3.0 kcal/mole at 25° and at the melting point (795°), respectively. Rossini and co-workers /21/ give L_{subl} = 65 kcal/mole at 700°.

Entropy of sublimation of MoO_3. According to Ueno /61/, ΔS_{subl} = 46.5 cal/mole · deg at 928.1°K. Rossini et al. /21/ give ΔS_{subl} = 67 cal/mole · deg at 700°.

Free energy of sublimation of MoO_3. According to Ueno /61/, ΔF_{subl} = 20.5 kcal/mole at 928.1°K. If the heat and entropy values of sublimation of Rossini et al. /21/ are used, the free energy of sublimation at 973°K is $\Delta F_{subl} = 65 - 0.067 \cdot 973 = 65 - 65.191 = -0.2$ kcal/mole.

Heat of dissociation of $(MoO_3)_3$. For the dissociation of $(MoO_3)_3 \rightarrow 3\,MoO_3$ ΔH = 220.9 kcal/mole /48/.

Entropy of dissociation of MoO_3*. Blackburn and co-workers /48/ give the energy of dissociation of gaseous MoO_3 into atomic molybdenum and oxygen as D_0^0 = 410.3 kcal/mole at 0°K. According to Brewer /44/, the energy of dissociation of gaseous MoO_3 into atoms is 445.0 ± 5 kcal/mole at 0°K.

Heat content of MoO_3. According to Cosgrove and Snyder /60/, the heat content of solid molybdenum trioxide is given by the equation:

$$H_T - H_{298} = 20.07T + 2.95 \cdot 10^{-3}T^2 + 3.68 \cdot 10^5 T^{-1} - 7481$$

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* [Energy of dissociation may be meant.]

and that of liquid molybdenum trioxide is given by:

$$H_T - H_{273} = 1.25151 \cdot 10^5 - 2.19714 \cdot 10^2 T + 1.47790 \cdot 10^{-1} T^2 - 2.33333 \cdot 10^{-5} T^3.$$

Entropy of MoO_3. From the data of Seltz /64/ on the heat capacity of MoO_3 from 70 to 299°K, Kelley /37/ calculated the following values for the entropy of MoO_3: $S^0_{70} = 2.97$ (this value was obtained by exptrapolation), $S^0_{298} - S^0_{70} = 15.71$ (this value was obtained by direct measurements), and $S^0_{298} = 18.7 \pm 0.3$ cal/mole · deg.

Rossini and co-workers /21/ give the entropy of MoO_3 as $S^0_{298} = 18.58$ cal/mole · deg.

Smith et al. /65/ calculated the entropy of solid MoO_3 at low temperatures; these data are presented in Table 85 /65/.

TABLE 85

Entropy of solid MoO_3 /65/

T, °K	S^0_T cal/mole · deg	T, °K	S^0_T cal/mole · deg	T, °K	S^0_T cal/mole · deg
10	0.048	120	6.195	230	14.251
20	0.197	130	6.965	240	14.919
30	0.450	140	7.733	250	15.574
40	0.811	150	8.497	260	16.219
50	1.286	160	9.253	270	16.853
60	1.857	170	10.000	273.15	17.050
70	2.499	180	10.737	280	17.476
80	3.189	190	11.463	290	18.090
90	3.916	200	12.178	298.15	18.580
100	4.665	210	12.881	300	18.686
110	5.427	220	13.572		

Free energy function of MoO_3. Smith et al. /65/ calculated the value of the functions $\Phi' = -\frac{F^\circ_T - H^\circ_0}{T} = -\frac{H_T - H^\circ_0}{T} + S^\circ_T$ and $\frac{H_T - H^\circ_0}{T}$ for solid MoO_3 at low temperatures. Their results are presented in Table 86.

TABLE 86

Variation of Φ' and $\frac{H^\circ_T - H^\circ_0}{T}$, cal/mole · deg

T, °K	Φ'	$\frac{H^\circ_T - H^\circ_0}{T}$	T, °K	Φ'	$\frac{H^\circ_T - H^\circ_0}{T}$	T, °K	Φ'	$\frac{H^\circ_T - H^\circ_0}{T}$
10	0.025	0.023	120	2.281	3.914	230	6.127	8.124
20	0.073	0.124	130	2.612	4.353	240	6.480	8.439
30	0.153	0.297	140	2.960	4.783	250	6.831	8.743
40	0.271	0.540	150	3.294	5.203	260	7.180	9.039
50	0.416	0.870	160	3.643	5.610	270	7.526	9.327
60	0.608	1.249	170	3.995	6.005	273.15	7.635	9.415
70	0.832	1.667	180	4.350	6.387	280	7.870	9.606
80	1.083	2.106	190	4.705	6.758	290	8.212	9.878
90	1.358	2.558	200	5.062	7.116	298.15	8.489	10.091
100	1.652	3.013	210	5.418	7.463	300	8.551	10.144
110	1.960	3.467	220	5.773	7.799			

Heat of formation of MoO_3. The heat of formation of MoO_3 from its elements is given in Table 87.

TABLE 87

Heat of formation of MoO_3

Heat of formation $-\Delta H^0_{298}$ kcal/mole	Method of determination	Year	Author	Reference
166.14	Direct determination at constant volume	1903	Delepine	/72/
167.0	Direct determination at constant pressure			
181.5	Calculated from the reaction $3Na_2O_2 + Mo = Na_2MoO_4 + 2Na_2O$	1910	Mixter	/73/
175.6	Direct determination	1924	Moose, Parr	/74/
180.4 ± 0.6	Direct determination recalculated for 19° at constant pressure	1934	Neumann, Kröger, Kunz	/75/
178.0	—	1955	Stasliewicz et al.	/51/

The most reliable values for the heat of formation of MoO_3 are the following: $\Delta H^0_{298} = -180.3 \pm 1.5$ kcal/mole /44/, $\Delta H^0_{298} = -178.2 \pm 1.5$ kcal/mole /22/, $\Delta H^0_{298} = -178.1$ kcal/mole /53/.

The reader can consider the value −178.1 kcal/mole as the most accurate for the purpose of calculation.

Entropy of formation of MoO_3. The entropy of formation ΔS^0_{298} of MoO_3, according to Brewer /44/, is −61.5 cal/deg·mole. Smith and coworkers /65/ give the value $\Delta S^0_{298} = -61.75$ e.u.

Free energy of formation of MoO_3. According to Brewer /44/, the free energy of formation ΔF^0_{298} of MoO_3 is −162 kcal/mole. According to Smith et al. /65/, $\Delta F^0_{298} = -161.92$ kcal/mole.

Kubaschewski and Evans /22/ give the following equation of the free energy of formation of MoO_3: $\Delta F^0_T = 38{,}700 - 19.5T$ from 298 to 1300°K. The accuracy of this equation is ± 3 kcal.

9. SULFIDES OF MOLYBDENUM

Molybdenum disulfide MoS_2 (M = 160.082)

Crystal structure of MoS_2. It has been established recently that MoS_2 exists in two modifications: natural MoS_2 (mineral molybdenite) and artificially prepared molybdenum disulfide.

Natural MoS_2 (α−MoS_2) has a hexagonal structure of type C_7^0. Its spatial group is D^4_{6h}. Parameters of the crystal lattice are a = 3.15 Å, c = 12.30 Å /76/.

Artificially prepared molybdenum disulfide (β-MoS_2) has a rhombohedric structure. The parameters of the crystal lattice are a = 3.17 Å and c = 18.38 Å.

The structure of β-MoS_2 was first investigated by Bell and Herfert /77/. The authors assumed that it corresponded to the $CdCl_2$ structure. Later, however, /78/, it was shown that the structure of β-MoS_2 is described by the spatial group $R_{3m} - C_{3v}^5$. Zelikman and co-workers /79/ studied the structure of MoS_2 samples, synthesized by means of five different methods. It was found that all samples had a layer-like structure, which, however, differed somewhat from both, α-MoS_2 (molybdenite) and β-MoS_2. β-MoS_2 does not occur in nature.

Density of MoS_2. The density of MoS_2 is given in Table 88.

TABLE 88

Density of MoO_3

Temperature, °C	Density, g/cm³	State	Year	Author	Reference
14	4.80	Crystalline	1901	Guichard	/80/
14	4.88	Amorphous			
—	5.05	Molybdenite	1925	Hassel	/81/

Heat of sublimation and decomposition of MoS_2. Molybdenum disulfide is the most stable of the molybden sulfides (MoS_2, Mo_2S_3, MoS_3).

Guichard /82/, Picon /83/, Montoro /84/, Joly /85/ showed that the behavior of MoS_2 depends on the conditions under which it is heated. Guichard /82/ observed that molybdenite heated for a short time in an electric arc furnace dissociated with formation of Mo_2S_3. On heating for longer periods of time molybdenite dissociates completely into metallic molybdenum [and sulfur]. Mo_2S_3 is formed when MoS_2 is heated in a crucible in the presence of air. Picon /83/ noted appreciable dissociation of MoS_2 in vacuo at 1100 to 1300°. Montoro /84/ and Guichard /86/ report that MoS_2 dissociates in vacuo at 1100° without formation of intermediate Mo_2S_3. When MoS_3 is heated in a carbon crucible at 1200°, dissociation of molybdenum disulfide proceeds to completion with the formation of metallic molybdenum within two hours.

Zelikman and Krein report in a later work /87/ that at atmospheric pressure MoS_2 dissociates appreciably only at temperatures exceeding 1300°; the probable dissociation product is Mo_2S_3.

Melting point of MoS_2. Zelikman and Belyaevskaya /88/ found that molybdenum disulfide (molybdenite) melts at 1650 to 1700° with simultaneous decomposition. Under these conditions the rate of dissociation of MoS_2 is very high and a lower sulfide (apparently Mo_2S_3) is formed as the intermediate product.

Dissociation pressure of MoS_2. Thermal dissociation of molybdenum disulfide at 800 to 1100° was studied by Zelikman and Krein /87/. They used an adaption of the dynamic method, described by Vol'skii /19/,

.n which the equilibrium constant K_{p_1} for the reduction of MoS_2 with hydrogen is determined:

$$MoS_2 + 2H_2 \rightleftarrows Mo + 2H_2S.$$

From the experimental values of $K_p = \frac{P_{H_2S}}{P_{H_2}}$ and from the equilibrium constant $K_{p_2} = \frac{P^2_{H_2} \cdot P_{S_2}}{P^2_{H_2S}}$ for the dissociation of hydrogen sulfide $2H_2S = 2H_2 + S_2$, the authors calculated the vapor pressure of sulfur $P_{S_2} = K_{p(3)}$ for reaction $MoS_2 \rightleftarrows Mo + S_2$; $K_{p(3)} = P_{(S_2)} = K^2_{p_1} \cdot K_{p(2)}$, or $\log P_{S_2} = 2 \log K_{p(1)} + \log K_{p(2)}$.

The mean experimental values of $K_{p(1)}$, the known values of $K_{p(2)}$ and the calculated values of $\log P_{S_2}$ are presented in Table 89.

TABLE 89

Dissociation pressure of MoS_2

Temperature, °C	$K_{p(2)} = \frac{V_{H_2S}}{V_{H_2}}$	$-2\log K_{p(1)}$	$-\log K_{p(2)}$	$-\log P_{S_2}$
800	0.0027	5.137	3.65	8.787
900	0.0083	4.162	2.90	7.062
1000	0.0120	3.842	2.25	6.092
1100	0.0319	2.992	1.75	4.742

Heat capacity of MoS_2. Andersen /89/ determined the true molar heat capacity of MoS_2 (natural molybdenite) at constant pressure. The mineral contained 0.31% FeS_2 and 0.58% SiO_2 as impurities. These were allowed for in the calorimetric determinations. The results are shown in Table 90.

TABLE 90

Heat capacity of MoS_2

Temperature, °K	Heat capacity cal/deg · mole	Temperature, °K	Heat capacity cal/deg · mole
56.1	2.297	161.3	10.57
60.7	2.601	189.5	11.78
70.5	3.264	220.4	13.28
80.6	3.944	249.5	14.14
100.2	5.764	279.7	14.88
118.7	7.368	292.7	15.08
143.5	9.318		

Kelley /90/ interpolated the data of Andersen /89/ and gave the following values for the heat capacity:

Temperature, °K	10	25	50	100	150	200	298.1	298
C_p, cal/deg · mole	(0.02)	(0.33)	(1.85)	5.72	9.79	12.57	15.19	15.17*

* According to Rossini and co-workers /21/.

Kelley /91/ used the data of Regnault /92/ to obtain the following equation for the variation of the molar heat capacity of solid MoS_2 with temperature:

$$C_p = 19.7 + 3.15 \cdot 10^{-3} T \text{ (at } 273 - 729°K).$$

Smith and co-workers /65/ determined the heat content of solid molybdenum disulfide calorimetrically /66, 67/ at low temperatures and from these results calculated the heat capacity. The calculated values are presented in Table 91.

TABLE 91

Heat capacity of solid MoS_2 according to Smith /65/, cal/mole·deg

T, °K	C_p	T, °K	C_p	T, °K	C_p
25.37	0.500	43.71	1.317	69.06	3.161
19.69	0.179	48.58	1.645	74.56	3.606
23.55	0.375	53.43	1.880	80.96	4.152
27.53	0.533	55.32	2.101	86.68	4.669
30.88	0.659	57.66	2.279	91.99	5.142
34.18	0.823	59.44	2.409	96.94	5.561
38.63	1.042	64.56	2.817	101.54	5.965

The rounded-off values of C_p for MoS_2 at temperatures of 20 to 90°K are given below:

Temperature, °K	20	30	40	50	60	70	80	90
C_p, cal/mole·deg	0.28	0.63	1.12	1.74	2.46	3.24	4.07	4.97

Entropy of MoS_2. From the heat-capacity data of Andersen /89/, Kelley /37/ calculated the entropy as $S^0_{56.2} = 1.04$ (extrapolated), $S^0_{298} - S^0_{56.2} = 14.00$ (measured) and $S^0_{298} = 15.0 \pm 0.2$ cal/mole·deg. Rossini and co-workers /21/ give the value $S^0_{298} = 15.1$ e.u. Smith and co-workers /65/ calculated the entropy of solid MoS_2 from their data on the heat capacity of MoS_2 from 20 to 90°K and obtained the following results:

Temperature, °K	20	30	40	50	60	70	80	90
Entropy S°_T, cal/mole·deg	0.140	0.315	0.560	0.870	1.25	1.69	2.17	2.71

Free energy function of MoS_2. Table 92 contains the values of the functions Φ' and of $\frac{H_T - H^0_0}{T}$, calculated by Smith et al. /65/, according to equation

$$\Phi' = -\frac{F^\circ_T - H^\circ_0}{T} = -\frac{H^\circ_T - H^\circ_0}{T} + S^\circ_T.$$

Heat of formation of MoS_2. The heat of formation of molybdenum disulfide was calculated from the following equation:

$$\Delta H^\circ_T = -57640 + 6.85T - 5.60 \cdot 10^{-3} T^2 - 0.503 \cdot 10^5 T^{-1},$$

and is $\Delta H^0_{298} = -56{,}270$ cal/mole. The foregoing equation was derived by Kelley /93/ on the basis of results obtained by Parravano and Malquori /94/.

Makolkin /95/ determined the heat of formation of MoS_2 as $\Delta H^0_{298} = 55{,}930$ cal/mole by studies of the electromotive force of galvanic cells. In another study, using analogous methods of measurement for the reaction $Mo(s) + 2S(rh) = MoS_2(s)$, Makolkin /96/ obtained the value $\Delta H^0_{298} = -55{,}910$ cal/mole.

Rossini and co-workers /21/ give the heat of formation of MoS_2 (s) as −55,500 cal/mole.

Entropy of formation of MoS_2. Makolkin /95/ determined the entropy of formation of MoS_2 experimentally and found $\Delta S^0_{298} = -6.608$ cal/deg·mole. In his reference book Kelley /93/ gives $\Delta S^0_{298} = -7.0$ cal/mole·deg.

TABLE 92

Functions Φ' and $\frac{H^\circ_T - H^\circ_0}{T}$ in cal/mole·deg. for solid MoS_2 /65/

T, °K	Φ'	$\frac{H_T - H^\circ_0}{T}$	T, °K	Φ'	$\frac{H_T - H^\circ_0}{T}$
20	0.055	0.085	60	0.42	0.83
30	0.110	0.205	70	0.57	1.12
40	0.19	0.37	80	0.74	1.43
50	0.29	0.58	90	0.93	1.78

Free energy of formation of MoS_2. From their results on the pressure of dissociation of MoS_2, Zelikman and Krein /87/ calculated the free energy of formation of this compound at various temperatures. The calculated results are given below:

Temperature, °C	800	900	1000	1100
Free energy $-\Delta F^\circ_T$, cal/mole	43140	37730	35480	29800

The equation for the variation of the free energy of formation of MoS_2 with temperature according to the equation Mo (s) + 2S (rh) = MoS_2 (s) was derived by Kelley /93/ from the experimental results of Parravano and Malquori /94/ and from data on the heat capacity of MoS_2:

$$\Delta F^\circ_T = -57,640 - 15.78\,T \log T + 5.60 \cdot 10^{-3} T^2 - 0.252 \cdot 10^5 T^{-1} + 49.24\,T. \qquad (I)$$

Makolkin /95/ determined the emf of the galvanic cell $Pt(H_2)KCl(0.01\,N) \| KCl(0.01\,N)/H_2S/MoS_2$, and obtained the value $\Delta F^0_{298} = -53,960$ cal/mole. Rossini et al. /21/ give the value $\Delta F^0_{298} = -53.8$ kcal/mole.

The equation for the free energy of formation of MoS_2 from molybdenum and gaseous sulfur can be obtained from Kelley's equation (I) above, by allowing for the free energy change for the sublimation of sulfur:

$$2S\,(rh) \rightleftharpoons S_2\,(g).$$

The free energy of formation of this reaction is:

$$\Delta F^\circ_T = 31,360 - 1.36\,T \log T + 5.8 \cdot 10^{-3} T^2 - 38.62\,T. \qquad (II)$$

Subtracting equation (II) from (I) gives

$$Mo\,(s) + S_2\,(g) = MoS_2\,(s),$$

$$\Delta F^\circ_T = -89,000 - 14.42\,T \log T - 0.2 \cdot 10^{-3} T^2 + 87.86\,T. \qquad (III)$$

Richardson and Jeffes /97/ give the following equation for the free energy of formation of molybdenum disulfide from its elements $Mo(s) + S_2 = MoS_2(s)$ from 1073 to 1373°K:

$$\Delta F_T^\circ = -52{,}560 + 10.2T \text{ cal/mole.}$$

Richardson and Jeffes /97/ estimate the accuracy of this equation as ±10%.

We consider that the equation of Kelley /93/ for ΔF_T^0 of MoS_2 is the best.

Molybdenum trisulfide MoS_3 (M = 192.148)

Vapor pressure of MoS_3. Parravano and Malquori /94/ studied the reaction $2MoS_3 = 2MoS_2 + S_2(g)$ from 628 to 691°K. The authors calculated partial pressures from equations for the reactions $S_8(g) = 4S_2(g)$ and $S_6(g) = 3S_2(g)$ and the results of these calculations are shown in Table 93.

TABLE 93

Dissociation pressure of MoS_3 /94/

Temperature, °K	Total pressure P_{tot}, atm.	Vapor pressure of sulfur P_{S2}
628	$5.26 \cdot 10^{-3}$	$6.86 \cdot 10^{-4}$
663	$3.79 \cdot 10^{-2}$	$3.37 \cdot 10^{-3}$
691	$2.35 \cdot 10^{-1}$	$1.20 \cdot 10^{-2}$

Entropy of MoS_3. The entropy of solid MoS_3 was calculated by Kelley /37/ from ΔS for the reaction of formation of MoS_3. Its value is given by $S_{298}^0 = 15.9 \pm 1.0$ kcal/mole · deg.

Heat of formation of MoS_3. Using the results of Parravano and Malquori /94/ and data for the reaction Mo + 3S (rh) = MoS_3, Kelley /93/ calculated the following approximate equation for the heat of formation of MoS_3 $\Delta H_T^0 = -60{,}440 - 3.5T$. The heat of formation from this equation is given by $\Delta H_{298}^0 = -61{,}480$ cal/mole.

Rossini et al. /21/ give the heat of formation of MoS_3 from its elements as $\Delta H_{298}^0 = -61{,}200$ cal/mole.

Entropy of formation of MoS_3. According to Kelley /93/, the entropy change for the reaction Mo + 3S (rh) = MoS_3 (s) is given by $\Delta S_{298}^0 = -13.8$ cal/mole · deg.

Free energy of formation of MoS_3. Kelley /93/ derived the approximate equation $\Delta F_T^0 = -60{,}440 + 8.1T \log T - 9.78T$ for reaction Mo + 3S (rh) = MoS_3. It leads to $\Delta F_{298}^0 = -57{,}380$ cal/mole.

Molybdenum sesquisulfide Mo_2S_3 (M = 288.098)

Entropy of Mo_2S_3. According to McCabe /98/, the standard entropy S_{298}^0 of Mo_2S_3 is 28.0 ± 2.0 cal/mole · deg.

Heat of formation of Mo_2S_3. McCabe /98/ gives the heat of formation of Mo_2S_3 as $\Delta H^0_{298} = -102.0 \pm 7.0$ kcal/mole.

Free energy of formation of Mo_2S_3. The free energy of formation of Mo_2S_3 for the reaction $2Mo\,(s) + 1\,1/2\,S_2\,(s) = Mo_2S_3\,(s)$ is given by the equation

$$\Delta F^\circ_T = -145{,}200 + 62.7T.$$

This equation is valid from 1300 to 1425°K. Its accuracy is ±9 kcal (McCabe /98/).

10. HALIDES OF MOLYBDENUM

Molybdenum hexafluoride MoF_6 (M = 209.95)

Melting point of MoF_6. Kubaschewski and Evans /22/ and Stull /20/ give the melting point of MoF_6 as 17°. The same temperature is given by Kelley /71/. Rossini et al. /21/ consider the best value to be 17.5° at P = 406 mm Hg.

Boiling point of MoF_6. The boiling point of this compound is approximately 36° (Kubaschewski and Evans /22/, Kelley /71/). Rossini and co-workers /21/ give the value 35°.

Sublimation temperature of MoF_6. Rossini and co-workers /21/ give the same value for the temperature of sublimation of MoF_6 as for its boiling point, i.e., 17.5° at 406 mm Hg.

Vapor pressure of MoF_6. Values for the vapor pressure of MoF_6 from 225 to 295°K were determined by Ruff and Ascher /99/. Their results relate to both solid and liquid MoF_6. The data on the vapor pressure of the liquid compound are more reliable than those on the solid compound. The data of Ruff and Ascher are quoted below /99/.

Temperature, °C	-89.5	-69.5	-44	-12.5	+3	16 (s)	36 (l)
Vapor pressure, atm. ..	0.0001	0.001	0.01	0.1	0.25	0.5	1.00

Values for the vapor pressure of MoF_6 interpolated by Stull /20/ are given below.

Temperature, °C.	-65.6	-49.0	-4.08	-32.0	-22.1	-16.2	-8.0	+4.1	17.2	36
Pressure, mm Hg.	1	5	10	20	40	60	100	200	400	760

The vapor pressure of liquid MoF_6 is expressed by the following equation

$$\log P = -\frac{1310}{T} + 7.12\,(T_{melt} - T_{boil})$$

derived by Kawakami /100/ and quoted by Kubaschewski and Evans /22/.

Heat of fusion of MoF_6. Kelley /71/ and also Kubaschewski and Evans /22/ give the heat of fusion of MoF_6 as 2500 cal/mole. Rossini et al. /21/ consider the most reliable value to be 2.2 kcal/mole, at a fusion temperature of 17.5° and a pressure of 406 mm Hg.

Entropy of fusion of MoF_6. Kelley /71/ gives for the entropy of fusion of this compound $\Delta S_{fus} = 8.62$ cal/mole · deg. Rossini and co-workers /21/ give $\Delta S_{fus} = 19.5$ cal/mole · deg. at t = 17.5° and P = 406 mm Hg.

Heat of vaporization of MoF_6. The heat of vaporization of MoF_6 at its boiling point (309°K) is given by L_{vap} = 6000 cal/mole /27/ and L_{vap} = 6.0 + 0.8 cal*/mole /22/. The same value is given by Rossini and co-workers /21/.

Entropy of vaporization of MoF_6. The entropy of vaporization of MoF_6 is given by ΔS^{vap}_{309} = 19.4 cal/mole · degree /27/ and ΔS_{vap} = 19.5 cal/mole · deg at t = 17.5° and P = 406 mm Hg /21/.

Free energy of vaporization of MoF_6. The free energy of vaporization of MoF_6 obeys the equation $\Delta F^0_T = 6000 - 19.4T$. Kelley /27/ calculated from this equation the value ΔF^0_{298} = 219 cal/mole.

Heat of sublimation of MoF_6. The heat of sublimation of MoF_6 is given as 8500 cal/mole at 25° /27/; 8500 ± 800 cal/mole at 25° /22/, and 8300 cal/mole at 17.5° and 406 mm Hg /21/.

Free energy of sublimation of MoF_6. According to Kelley /27/, the free energy of sublimation of MoF_6 is expressed by the relation $\Delta F^0_T = 8500 - 28.03T$, hence ΔF^0_{298} = 144 cal/mole.

Entropy of MoF_6. Kubaschewski and Evans /22/ give the standard entropy as ΔS^0_{298} = 79.0 ± 3.0 cal/mole · degree.

Heat of formation of MoF_6. Kubaschewski and Evans /22/ give for the heat of formation of this compound the approximate value ΔH^0_{298} = −450 kcal/mole.

Molybdenum hexachloride $MoCl_6$ (M = 308.692)

Heat of formation of solid $MoCl_6$. Molybdenum hexachloride is a rather unstable compound. If chlorine reacts with molybdenum, only $MoCl_5$ is formed. Data on the heat of formation of $MoCl_6$ are doubtful and need checking.

Rossini and co-workers /21/ give ΔH^0_{298} = −90.0 kcal/mole for the heat of formation of solid $MoCl_6$.

Molybdenum pentachloride $MoCl_5$ (M = 273.235)

Density and molar volume of $MoCl_5$. According to Biltz and Fendius /101/, the density of this compound at 25° is 2.9275 g/cm^3. The same authors /101/ give the molar volume of $MoCl_5$ as 93.3 cm^3/mole.

Melting point of $MoCl_5$. The melting point of $MoCl_5$ is approximately 194° /21, 22/.

Boiling point of $MoCl_5$. The boiling point of $MoCl_5$ is 268° /21, 22/.

Vapor pressure of $MoCl_5$. For the variation of the vapor pressure of $MoCl_5$ with absolute temperature Childs et al. /102/ give the following equation valid from 298°K to the boiling point

$$\log P(\text{mm Hg}) = -\frac{5210}{T} + 13.1.$$

Heat of fusion of $MoCl_5$. Brewer et al. /103/ give L_{fus} = 8.0 kcal/mole.

Heat of vaporization of $MoCl_5$. Kubaschewski and Evans /22/ considered the best value of the heat of vaporization at the boiling point to be 15.0 ± 3.5 kcal/mole.

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* [Probably kcal is intended.]

Heat of sublimation of $MoCl_5$. Kubaschewski and Evans /22/ give the heat of sublimation of $MoCl_5$ at its melting point as $L_{subl} = 23.5 \pm 3.0$ kcal/mole.

Entropy of $MoCl_5$. According to Brewer et al. /103/, the standard entropy of $MoCl_5$ is given by $S^0_{298} = 65.0 \pm 5.0$ cal/mole · degree.

Heat of formation of $MoCl_5$. Gmelin /104/ gives the heat of formation of $MoCl_5$ according to reaction $Mo\,(s) + \frac{5}{2} Cl_2 = MoCl_5\,(s)$ as $\Delta H^0_{298} = 90.8$ kcal/mole. Brewer and co-workers /103/ and Rossini and co-workers /21/ give the value $\Delta H^0_{298} = -90.8 \pm 2.5$ kcal/mole.

Other chlorides of molybdenum, $MoCl_4$, $MoCl_3$, and $MoCl_2$

Heats of formation of $MoCl_4$, $MoCl_3$, and $MoCl_2$. The values for the heats of formation ($-\Delta H^0_{298}$ kcal/mole) of solid $MoCl_4$, $MoCl_3$, and $MoCl_2$, as given by Rossini and co-workers /21/, are presented below:

$MoCl_4$	79
$MoCl_3$	65
$MoCl_2$	44

Bromides of molybdenum, $MoBr_5$, $MoBr_4$, $MoBr_3$, and $MoBr_2$

Heats of formation of solid $MoBr_5$, $MoBr_4$, $MoBr_3$, and $MoBr_2$. Rossini et al. /21/ give the following values for the heats of formation of the bromides of molybdenum ($-\Delta H^0_{298}$, kcal/mole).

$MoBr_5$	51
$MoBr_4$	45
$MoBr_3$	41
$MoBr_2$	29

Iodides of molybdenum, MoI_5, MoI_4, MoI_3, and MoI_2

Heats of formation of solid MoI_5, MoI_4, MoI_3, and MoI_2. Rossini et al. /21/ give the following values for the heats of formation ($-\Delta H^0_{298}$, kcal/mole) of the solid molybdenum iodides

MoI_5	18
MoI_4	18
MoI_3	15
MoI_2	12

11. CARBIDES OF MOLYBDENUM

Molybdenum carbide Mo_2C (M = 203.9)

Crystal structure of Mo_2C. Molybdenum carbide Mo_2C has a hexagonal structure with the following lattice constants a = 3.00 Å and b = 4.72 Å (Kubaschewski and Evans /22/).

Density of Mo_2C. The density of Mo_2C was calculated from X-ray data by Lester and Gregg /105/ and found to be 9.901 g/cm^3. Weibke /106/ gives the value 9.15 g/cm^3.

Hardness of Mo_2C. The hardness of Mo_2C is 7 (Mohs hardness scale), according to Friedrich and Sittig /107/.

Melting point of Mo_2C. The melting point of Mo_2C is given as 2960 ± 50°K by Agte and Alterthum /108/, 2690°C by Kubaschewski and Evans /22/, and 2945°K by Rossini et al. /21/.

Entropy of Mo_2C. The entropy is given by S^0_{298} = 20.4 cal/mole · deg. Kelley /109/ gives an approximate value of 19.8 cal/mole · deg. Rossini and co-workers /21/ consider the most reliable value to be 19.7 cal/mole · deg.

Heat of formation of Mo_2C. For the heat of formation of Mo_2C, in the reaction 2Mo (s) + C (β-graphite) = Mo_2C, Kelley /109/ gave ΔH^0_{298} = 4200 cal/mole. Kubaschewski and Evans /22/, referring to the work of Kelley /109/, also give ΔH^0_{298} = 4.2 kcal/mole. Rossini and co-workers /21/ give ΔH^0_{298} = 4.3 kcal/mole.

Entropy of formation of Mo_2C. Kelley /109/ calculates the entropy of formation ΔS^0_{298} of Mo_2C as 4.8 cal/mole · degree.

Free energy of formation of Mo_2C. According to Kelley's calculations /109/, the free energy of formation of Mo_2C is given by equation $\Delta F^0_T = 4200 - 4.80T$, from which ΔF^0_{298} = 2770 cal/mole. Kubaschewski and Evans /22/ quote Richardson /110/ and give ΔF^0_T = 6700 cal/mole for the reaction Mo_2C (s) = 2Mo (s) + C (s). This value may be used from 298 to 1273°K.

Rossini and co-workers /21/ give ΔF^0_{298} = 2900 cal/mole.

Molybdenum carbide MoC (M = 107.95)

Density of MoC. According to Moissan and Hoffmann /111/, the density of MoC at 20° is 8.4 g/cm^3.

Hardness of MoC. According to the same authors /111/, the hardness of MoC is between 7 and 9 (Mohs Scale).

Melting point of MoC. According to Agte and Alterthum /108/, the melting point of MoC is 2965 ± 50°K. Greenwood /112/ and Rossini and co-workers /21/ give 2687° and 2677°, respectively.

12. MOLYBDENUM NITRIDE Mo_2N (M = 205.908)

Heat capacity of Mo_2N. Kelley /40/ gives the following equation for the heat capacity of Mo_2N from 298 to 800°K:

$$C_p = 11.19 + 13.80 \cdot 10^{-3}T.$$

The accuracy of this equation is ±3%. The equation is based on the data of Sato /113/ for the heat content of Mo_2N,

Heat content of Mo_2N. Using the data of Sato /113/, Kelley /40/ determined the heat contents of Mo_2N from 400 to 800°K with a mean accuracy of ±3%. His values are quoted below:

Temperature, °K	400	500	600	700	800
Heat content $H_T - H^\circ_{298}$ cal/mole	1610	3360	5280	7290	9370

Kelley /40/ also derived the following equation:

$$H_T - H_{298} = 11.19T + 6.90 \cdot 10^{-3}T^2 - 3950.$$

Entropy of Mo_2N. For the standard entropy of Mo_2N, Kubaschewski and Evans /22/ give as an approximation $S^0_{298} = 21.0$ cal/mole · degree. The entropy of Mo_2N at various temperatures /40/ is given below:

Temperature, °K	400	500	600	700	800
Entropy $S_T - S^\circ_{298}$ cal/mole · deg	4.64	8.54	12.03	15.13	17.19

Heat of formation of Mo_2N. Neuman, Kröger, and Kuntz /75/ determined the heat of reaction for $2Mo\,(s) + \frac{1}{2}N_2 = Mo_2N$. They found $\Delta H^0_{298} = -16{,}600 \pm 600$ cal/mole. For the heat of formation of Mo_2N, Kubaschewski and Evans /22/ give $\Delta H^0_{298} = -16.6 \pm 0.5$ kcal/mole.

13. OXIDATION AND REDUCTION REACTIONS OF MOLYBDENUM COMPOUNDS

Reduction of molybdenum oxides by hydrogen.

The reduction of molybdenum oxides by hydrogen was studied by Chaudron /114/ in 1921 and by Tonosaki /115/ in 1940. Their publications are the earliest on this subject.

Chaudron /114/ used a static method to study the equilibrium of the reduction of molybdenum dioxide by hydrogen $MoO_2 + 2H_2 \rightleftharpoons Mo + 2H_2O$ from 700 to 1100° and calculated its equilibrium constant $K_p = \frac{P_{H_2O}}{P_{H_2}}$.

Reaction equilibria were reached both from the oxidation and reduction sides. The experimental values of K_p at various temperatures are given in Table 94.

Tonosaki /115/ used a static method to study the reduction of molybdenum dioxide by hydrogen: $\frac{1}{2}MoO_2 + H_2 \rightleftharpoons \frac{1}{2}Mo + H_2O\,(g)$ from 645 to 823°K. The author established the following relationship between $K_p = \frac{P_{H_2O}}{P_{H_2}}$ and T:

$$\log K_p = -\frac{1444.6}{T} + 0.9413.$$

Tonosaki /115/ also calculated the heat and the free energy [of formation] for this reaction. He gave $\Delta H^0_{298} = 7973$ cal and $\Delta F^0_{298} = 5909$ cal.

The data of Chaudron /114/ and Tonosaki /115/ are believed to be insufficiently accurate.

TABLE 94

Variation of the equilibrium constant K_p for the reaction $MoO_2 + 2H_2 \rightleftharpoons Mo + H_2O$ with temperature /114/

Temperature, °C	Equilibrium constant K_p		Temperature, °C	Equilibrium constant K_p	
	reduction	oxidation		reduction	oxidation
700	0.37	0.39	950	0.72	—
760	0.45	0.47	985	0.86	0.87
850	0.56	0.57	1040	0.97	1.00
940	—	0.71	1100	1.12	1.13

In 1957, Hegedüs, Sasvary, and Neugebauer /43/, using the dynamic method [see ref. 43] and employing X-ray techniques, studied the reduction of molybdenum trioxide by hydrogen from 300 to 760°. They found that the reduction of MoO_3 by hydrogen proceeds in four stages and four intermediate products are formed:

from 390—670°

$$MoO_3 + H_2 \rightarrow MoO_{2.98} + H_2O,$$

from 360—660°

$$MoO_{2.98} + H_2 \rightarrow MoO_{2.75} + H_2O,$$

from 350—650°

$$MoO_{2.75} + H_2 \rightarrow MoO_2 + H_2O,$$

from 500—690°

$$MoO_2 + H_2 \rightarrow Mo + H_2O.$$

Reduction of molybdenum disulfide by hydrogen.

The reduction of molybdenum disulfide by hydrogen from 1078 to 1373°K, according to the reaction $MoS_2 + H_2 \rightleftharpoons Mo + 2H_2S$, was studied by Parravano and Malquori /94/, utilizing a flow method (Jellinek's method).

They found the following values of the equilibrium constant: $\left(K_p = \frac{p^2_{H_2S}}{p^2_{H_2}}\right)$

Temperature, °K	1078	1183	1278	1373
$K_p = \frac{p^2_{H_2S}}{p^2_{H_2}}$	$3.41 \cdot 10^{-5}$	$7.66 \cdot 10^{-5}$	$1.88 \cdot 10^{-4}$	$3.66 \cdot 10^{-4}$

From the fact that $K_p = \frac{p^2_{H_2S}}{p^2_{H_2}}$ is a constant at 1078°K, Parravano and Malquori /94/ concluded that the reduction of MoS_2 by hydrogen proceeds in one stage without formation of the intermediate compound Mo_2S_3. The absence of Mo_2S_3 was later confirmed by Montoro /84/, using X-ray analysis.

From the experimental data of Kelley /94/, the heat capacity difference ΔC_P and the heat, entropy, and free energy of the reaction $MoS_2 + 2H_2 \rightleftharpoons Mo + 2H_2S$ are as follows:

$$\Delta C_P = -12.95 + 3.75 \cdot 10^{-3} T - 0.503 \cdot 10^5 T^{-2}, \quad \text{(I)}$$

$$\Delta H_T = \Delta H_0 - 12.95T + 1.88 \cdot 10^{-3} T^2 + 0.503 \cdot 10^5 T^{-1}, \quad \text{(II)}$$

$$\Delta S^\circ_T = -12.95 - 29.82 \log T + 3.75 \cdot 10^{-3} T + 0.252 \cdot 10^5 T^{-2}, \quad \text{(III)}$$

$$\Delta F^\circ_T = \Delta H_0 + 29.82T \log T - 1.88 \cdot 10^{-3} T^2 + 0.252 \cdot 10^5 T^{-1} + IT. \quad \text{(IV)}$$

The standard entropy of the reaction, ΔS^0_{298} = 27.5 cal/mole · degree, was calculated from the following data: S^0_{298} = 6.8 for molybdenum, S^0_{298} = 49.15 for H_2S, S^0_{298} = 15.1 for MoS_2, and S^0_{298} = 31.33 cal/mole·degree for H_2. Substituting in equation* (III) ΔS^0_{298} = 27.5 cal/mole · degree and T = 298°K gives −112.8 cal/mole · degree for ΔH_0. Since ΔH_0 varies with temperature, an average value of 50,200 cal/mole was calculated for the range 1078 to 1373°K. Substituting this value for ΔH_0 and the value I = −112.88 cal/mole degree in equations (II) and (IV) for reaction $MoS_2 + 2H_2 \rightleftharpoons Mo + 2H_2S$, the following equations are obtained:

$$\Delta H^\circ_T = 50{,}200 - 12.95T - 1.88 \cdot 10^{-3} T^2 + 0.503 \cdot 10^5 \cdot T^{-1},$$

$$\Delta F^\circ_T = 50{,}200 + 29.82\, T \log T - 1.88 \cdot 10^{-3} T^2 + 0.252 \cdot 10^5 T^{-1} - 112.88T,$$

hence

$$\Delta H^\circ_{298} = 46{,}670 \text{ cal/mole and } \Delta F^\circ_{298} = 38{,}460 \text{ cal/mole.}$$

Reduction of molybdenum carbide by hydrogen

Schenk and co-workers /116/ studied the reduction of Mo_2C by hydrogen $Mo_2C + 2H_2 \rightleftharpoons 2Mo + CH_4$ and determined the equilibrium constants $K_p = \frac{P^2_{H_2}}{P_{CH_4}}$ for two temperatures: 973 and 1123°K. At 973°, K_p = 3.55, at 1123°, K_p = 18.5. The values ΔH_0 = 21,500 cal/mole and I = −7.29 cal/mole degree were also calculated by these authors. The heat and free energy of this reaction are given by

$$\Delta H^\circ_T = 21{,}500 + 2.5T,$$

$$\Delta F^\circ_T = 21{,}500 - 5{,}8\, T \log T - 7.29T,$$

hence

$$\Delta H^\circ_{298} = 22{,}250 \text{ cal/mole and } \Delta F^\circ_{298} = 15{,}050 \text{ cal/mole.}$$

Reduction of molybdenum dioxide by carbon monoxide

According to Spencer and Justice /117/, molybdenum dioxide is reduced to molybdenum carbide (Mo_2C) by CO according to the following equation:

$$2MoO_2 + 6CO = Mo_2C + 5CO_2.$$

The equilibrium constant for this reaction is 1.44 at 810°C.

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* [The following is not clear in the Russian text.]

Oxidation of molybdenum disulfide by oxygen

The mineral molybdenite MoS_2 is rapidly oxidized to MoO_3 by oxygen at temperatures above 450 or 500°, according to reaction

$$MoS_2 + 3^1/_2O_2 = MoO_3 + 2SO_2.$$

The actual process proceeds in stages and the equation mentioned above is only for the overall reaction. It has been investigated by Glemser and Lutz /118/, who gave its heat of reaction as $\Delta H^0_{298} = -266.24$ kcal.

Chapter 3

THERMODYNAMIC PROPERTIES OF TITANIUM AND OF ITS MORE IMPORTANT COMPOUNDS

14. METALLIC TITANIUM (M = 47.90)

Crystal structure, density, and melting point

Isotopes of titanium. Using a mass-spectrometer, Aston /1/ found four isotopes of titanium, i.e., Ti^{46}, Ti^{47}, Ti^{49}, and Ti^{50} besides the main isotope Ti^{48}. Data on these isotopes are presented in Table 95.

TABLE 95

Isotopes of titanium

Mass of isotope	Content of isotope, %	Atomic weight of titanium in this mixture
46	7.90	47.91
47	7.75	
48	73.45	
49	5.51	
50	5.34	

Two unstable isotopes of titanium were also observed: Ti^{45} and Ti^{51}.

Crystal structure of titanium. Metallic titanium exists in two allotropic modifications. The low-temperature or α-form has a close-packed hexagonal lattice; the high temperature or β-form has a body-centered cubic lattice. The transition point of the α- to β-modification occurs at 882.5°.

Lattice parameters of α-titanium. Lattice parameters a and c of the hexagonal unit cell of α-titanium, according to various authors, are given in Table 96.

The most accurate data on the dimension of the unit cell of α-titanium at room temperature are those of Clark /2/.

The average values of the parameters of the unit cells of α-titanium, calculated by Clark /2/ from four separate determinations on various samples at 25 ± 2°, are as follows: a = 2.9503 ± 0.0004 Å, c = 4.6831 ± 0.0004 Å, c/a = 1.5873 ± 0.0004.

TABLE 96

Lattice parameters of α-titanium at room temperature

a	c	c/a	Year	Author	Reference
2.9503	4.6831	1.587	1949	Clark	/2/
2.9496	4.6282	1.587	1953	Berry, Raynor	/3/
(2.945)	(4.679)	1.588	1952	Rostoker	/4/
2.9504	4.6834	1.587	1950	Finlay, Snyder	/5/
2.952	4.695	1.591	1949	Litton, Gonser	/6/
2.951	4.68	1.59	1939	Fast	/7/
2.9509	4.6904	1.5907	1949	Greiner, Ellis	/8/
2.953	4.730	1.602	1936	Burgers, Jacobs	/9/
2.953	4.729		1930	Hägg	/10/

* Note. The values in brackets are only approximate values.

Lattice parameters of β-titanium. Lattice parameters of the body-centered cubic cell of β-titanium at various temperatures are given in Table 97.

TABLE 97

Lattice parameters of β-titanium at various temperatures

Temperature, °C	Parameter a, Å	Author	Reference
900	3.32	Burgers, Jacobs	/ 9/
900 ± 5°	3.3132	Eppelsheimer, Penman	/11/
room temperature	3.283 ± 0.003*	Levinger	/12/
as above	3.29**	Adenstedt, Pequignot, Raymer	/13/

* Data obtained by extrapolation.

** Calculated data.

Density of α- and β-titanium. The densities of α- and β-titanium have been calculated by numerous authors. Hunter /14/, Patterson /15/, and Hevesy /16/ give densities of 4.50, 4.49, and 4.50 g/cm^3, respectively, for 99.9% α-titanium at 20°. Luchinskii /17/ gives the density of α-titanium at 20° as 4.512 g/cm^3.

The density of α-titanium at 25 ± 2° was calculated by Clark /2/ from accurate data on the lattice spacing to be 4.505 g/cm^3. Fast /7/ determined the density of α-titanium by pycnometric methods and obtained the average value 4.507 ± 0.005 g/cm^3.

According to Burgers and Jacobs /9/, β-titanium at 20° has a density of 4.31 g/cm^3. According to the same authors the density of β-titanium at 900° is 4.32 g/cm^3. These values were calculated from lattice parameters of impure metal at high temperatures.

According to Blocher and Campbell /18/, the density of β-titanium is 4.35 g/cm^3, i.e., somewhat higher than the value given above. Their method consisted in observing the sagging of a heated titanium hair at 900°.

Atomic volume of titanium. Weiss and Kaiser /19/, Hevessy /16/, and Biltz and Maisel /20/ gave the atomic volume of solid titanium as 9.3, 10.93, and 10.7 cm^3/g · atom, respectively.

Coefficient of thermal expansion of solid titanium. According to Hidnert /21/, the coefficient of linear thermal expansion of solid titanium increases continuously from $5 \cdot 10^{-6}$ degree^{-1} at 150° to $12 \cdot 10^{-6}$ degree^{-1} at 565°. The coefficient of linear thermal expansion of solid titanium at 20° is taken as $7.14 \cdot 10^{-6}$ degree^{-1}.

The coefficient of linear expansion of polycrystalline titanium has also been measured by Erfling /22/, Fast /7/, and Greiner and Ellis /8/. All authors with the exception of Fast /7/ used titanium samples containing impurities. For this reason the result of these authors /21, 22, 8/ are only approximate. McQuillan /23/ is of the opinion that the most probable value for the coefficient of linear expansion of polycrystalline titanium is $(8.35 \pm 0.15) \cdot 10^{-6}$ degree^{-1} at 15°.

According to /6/ the coefficient of linear expansion from 15 to 730° is $(8.8 \text{ to } 9.2) \cdot 10^{-6}$ degree^{-1}. According to Berry and Raynor /3/, the average coefficients of linear expansion in the direction of the axes a and c are $11.03 \cdot 10^{-6}$ and $13.37 \cdot 10^{-6}$ degree^{-1}, respectively. These data are confirmed by the results of Erfling /22/, who found that the expansion of titanium in the direction of the c axis is 20% higher than that in the direction of the a axis.

$\alpha \rightleftharpoons \beta$ Titanium transition temperature. The $\alpha \rightleftharpoons \beta$ titanium transition temperature is at 880° (Kroll /24/, Burgers and Jacobs /9/) or 885 ± 10° (Fast /25/). DeBoer, Burgers, and Fast /26/ gave the transition temperature as 880 ± 20°; these authors observed a sharp change in the specific resistance of titanium at the given temperature. The determination was carried out using a wire which was heated to the transition temperature by means of an electric current passed through it. Other authors also observed an abrupt change in the physical properties of titanium at the transition temperature. This change in properties was used to determine the specific resistance of this metal.

McQuillan /27/ is of the opinion that his data obtained by various independent methods are the most accurate. The author gives a transition temperature of 882.5 ± 0.5%, which is within the limits of experimental error given by other authors.

Data of various authors are presented in Table 98.

Rossini and co-workers /32/ and Stull and Sinke /33/ give 882° for the $\alpha \rightleftharpoons \beta$ titanium transition.

Melting point of titanium. The melting point of titanium, as determined by various authors, is given in Table 99.

It can be seen from Table 99 that before 1950 it was assumed that the melting point of titanium was between 1725 and 1800°. Quite recent papers have shown, however, that it is considerably lower. Previous measurements had been carried out on titanium containing such impurities as oxygen, nitrogen, carbon, etc., which earlier workers were unable to remove.

With the exception of Oriani, the investigators all determined the melting point of titanium with an optical pyrometer. Oriani used as a sample

a suspended titanium wire which was a part of a heated loop. The temperature at which the wire melted was determined by means of an optical pyrometer. The most reliable values are apparently those of Schöfield /48/ and Oriani and Jones /47/.

Rossini et al. /32/ give the melting point of titanium as 1678°.

TABLE 98

Titanium transition temperature

Transition temperature, °C	Method	Year	Author	Reference
882.5 ± 1.0	Specific resistance and hydrogen pressure	1950—1951	McQuillan	/28/
From 883 to 887	emf measurements	1951	Worner	/29/
882 ± 4	Thermal analysis	1951	Duwez	/30/
884 ± 3.5	Thermal analysis	1953	Edwards, Johnston Ditmars	/31/
882.5 ± 0.5	Thermodynamic calculations	1950	McQuillan	/27/

TABLE 99

Melting point of titanium

Melting point, °C	Year	Author	Reference
1800—1850*	1910	Hunter	/14/
2200—2400	1910	Weiss, Kaiser	/19/
2700**	1910	Ruff	/34/
1795 ± 15	1913	Burgers, Waltenberg	/35/
2000	1919	Guertler, Pirani	/36/
1802	1941	Luchinskii	/17/
1725†	1946	Kroll, Schlechten	/37/
1725†	1946	Din et al.	/38/
1725†	1948	Waggang, Gi	/39/
1725†	1948	Greiner, Ellis	/40/
1725†	1949	Gonser	/41/
1725†	1949	Stewart	/42/
1723 ± 20 ††	1949	Lytton, Gonser	/6/
1716 ± 25	1951	Hansen, Kamen, Kessler, McPherson	/43/
1690 ± 10	1951	Ogden, Maykuth, Finlay, Jaffee	/44/
1696 ± 15	1952	Adenstedt, Pequignot, Raymer	/13/
1680 ± 10	1953	Maykuth, Ogden, Jaffee	/45/
1660 ± 10	1953	Schöfield, Bacon	/46/
1672 ± 4	1954	Oriani, Jones	/47/
1665 ± 5	1954	Schöfield	/48/
1668 ± 10	1956	Deardorff, Hayes	/49/

* Titanium containing approximately 5%C.

** Titanium with traces of iron.

† Magnesium-reduced titanium.

†† Iodide titanium.

Boiling point of titanium. Table 100 contains values for the boiling point of titanium as determined by various authors.

TABLE 100

Boiling point of titanium

Temperature, °C	Year	Author	Reference
2800	1916	Van-Laar	/50/
3400	1918	Mott	/51/
3260	1947,1949	Blocher, Campbell	/52/
3500	1958	A. D. McQuillan, M. K. McQuillan	/23/

Luchinskii /17/ gives a value above 3450°, Stull and Sinke /33/ give 3550°. It seems that the last value is the most reliable and should be used for thermodynamic calculations.

Vapor pressure of titanium. The authors listed below used the Langmuir method based on measuring the rate of vaporization of a wire sample at different temperatures.

Blocher and Campbell /52/ determined the vapor pressure of titanium from 1500 to 1800°K using the Langmuir method and their results are presented in Table 101.

TABLE 101

Vapor pressure of titanium

Temperature, °K	Time, sec	Rate of vaporization*, $g/cm^2 \cdot sec$	Vapor pressure*, atm.
1510	144000	$1.62 \cdot 10^{-8}$; $1.80 \cdot 10^{-8}$	$2.05 \cdot 10^{-9}$; $2.28 \cdot 10^{-9}$
1613	39300	$1.60 \cdot 10^{-7}$; $1.86 \cdot 10^{-7}$	$2.08 \cdot 10^{-8}$; $2.42 \cdot 10^{-8}$
1636	21120	$2.90 \cdot 10^{-7}$; $3.10 \cdot 10^{-8}$	$3.80 \cdot 10^{-8}$; $4.10 \cdot 10^{-8}$
1727	4800	$1.33 \cdot 10^{-6}$; $1.37 \cdot 10^{-7}$	$1.79 \cdot 10^{-7}$; $1.86 \cdot 10^{-7}$
1822	1050	$9.20 \cdot 10^{-6}$; $8.90 \cdot 10^{-6}$	$1.28 \cdot 10^{-6}$; $1.24 \cdot 10^{-6}$

* The values in the first column were obtained by measuring the resistance of a titanium wire, those of the second column by calculating the decrease in weight of this wire.

According to Blocher and Campbell /52/, the variation of vapor pressure with temperature from 1500 to 1800°K is given by the equation:

$$\log P = 7.782 - \frac{24.275}{T} - 0.00023T.$$

Carpenter and Mair /53/ investigated the rate of vaporization of titanium from 1650 to 1810°K.

According to these investigators /53/, the variation in vapor pressure with temperature, as calculated from the rate of vaporization of titanium, is given by the following equation:

$$\log P = 7.30 - \frac{24{,}200}{T}.$$

Edwards and co-workers /31/, using the Langmuir method, measured the vapor pressure of titanium from 1587 to 1764°K. Their results are presented in Table 102.

TABLE 102

Vapor pressure of titanium /31/

No. of sample	Temperature, °K	Time, sec	Total loss in weight, g	Effective surface, cm^2	Rate of vaporization $g \cdot cm^{-2} sec^{-1} \cdot 10^8$	Vapor pressure, $atm \cdot 10^8$
8	1587	24,652	0.0233	15.8993	5.952	0.773
7	1624	6890	0.01557	15.9284	14.187	1.864
1	1651	4493	0.001749	15.9709	24.374	3.228
6	1667	4846	0.002473	15.9800	31.935	4.251
2	1675	2983	0.001803	15.9748	37.836	5.047
5	1698	3438	0.003261	16.0987	58.918	7.914
3	1725	1895	0.002988	16.1529	97.916	13.245
9	1764	2185	0.007366	16.1206	191.907	26.269

The vapor pressure of titanium /31/ in the given temperature range is given by the following equation

$$\log P\,(\text{atm}) = 7.7960 - \frac{24.644}{T} - 0.000227T.$$

Vickery /54/ determined the constants A and B for liquid and solid titanium in the simplified vapor pressure equation: $\log P\,(\text{mm Hg}) = A - \frac{B}{T}$. These constants are $A = 3.810$, $B = 2472$, and $A = 3.350$, $B = 1525$ for solid and liquid titanium, respectively.

From experimental data Blocher and Campbell /18/ derived the following empirical equations for the variation in the vapor pressure of solid and liquid titanium with temperature:

$$\log P = \frac{24{,}275}{T} - 0.23 \cdot 10^{-3} \cdot T + 10.66 \quad (1200 - 2000°\text{K}),$$

$$\log P = -\frac{22{,}110}{T} + 9.135 \quad (T_m - T_b).$$

By extrapolation of the vapor pressure curve of titanium to its melting point (2000 ± 10°K), Van Arkel /55/ obtained a vapor pressure of $1.2 \cdot 10^{-2}$ mm Hg at this temperature. Rossini and co-workers /32/ give the vapor pressure of titanium at 1812° as 0.036 mm Hg.

Heat capacity, heat of transition, sublimation, fusion, and vaporization, free energy of sublimation, and entropy of transformation of titanium

Heat capacity of titanium. Data of Kelley /56/ on the specific and atomic heat capacities of ductile titanium prepared by reduction of titanium tetrachloride with sodium at low temperatures are presented in Table 103.

TABLE 103

Specific and atomic heat capacities of titanium /56/

Temperature, °C	Atomic heat capacity, cal/g·atom·deg	Specific heat capacity, cal/g·deg	Temperature, °C	Atomic heat capacity, cal/g·atom·deg	Specific heat capacity, cal/g·deg
-219.5	1.278	0.0266	-88.8	5.142	—
-202.5	2.142	—	-68.3	5.355	0.1118
-189.2	2.737	0.0571	-48.1	5.538	—
-170.1	3.460	—	-28.1	5.683	0.1184
-149.8	4.061	0.0848	- 7.3	5.822	—
-129.6	4.516	—	+12.8	5.951	
-109.1	4.879	0.1018	+22.1	5.948	0.1249

Kelley /56/ determined the specific heat capacity of titanium in the range of 53.5 to 295.1°K in samples containing 98.75% of titanium. Kothen and Johnson /57/, using high purity titanium samples, repeated Kelley's experiment /56/ and found the following atomic heat capacities at 15.4 to 305.5°K (Table 104):

TABLE 104

Atomic heat capacity of titanium /57/

Temperature, °K	Specific heat capacity, cal/g·atom·deg	Temperature, °K	Specific heat capacity, cal/g·atom·deg	Temperature, °K	Specific heat capacity, cal/g·atom·deg
15	0.040	125	4.155	225	5.539
25	0.157	150	4.684	250	5.713
50	1.136	175	5.043	275	5.864
75	2.402	200	5.321	298.16	5.976
100	3.434				

McQuillan /23/ gives the specific heat capacity of titanium as 0.1248 ± 0.0002 cal/g·degree at 15°.

Jaeger et al. /58/ give the following values for the atomic heat capacity of titanium at various temperatures:

t °C	C_p, cal/g·atom·deg
200	6.507
817	8.901
905	10.280

The average specific and atomic heat capacities of titanium are presented in Table 105.

Table 106 contains the heat capacities of solid, liquid, and gaseous titanium, as given by Stull and Sinke /33/.

Rossini and co-workers /32/ give heat capacities of 6.010 and 5.8385 cal/g·atom·degree for solid and gaseous titanium, respectively.

Kelley /61/ derived the following equation for the atomic heat capacity:

$$C_p = 8.91 + 1.14 \cdot 10^{-3} \cdot T - 4.33 \cdot 10^{5} \cdot T^{-2}.$$

TABLE 105

Average specific and atomic heat capacities of titanium

t, °C	C_p cal/deg·g	C_p cal/g·atom·deg	Year	Author	Reference
-185 – + 20	0.0824	–	1907	Nordmeyer, Bernoulli	/59/
100 and higher	0.1418	6.830	1910	Weiss, Kaiser	/19/
0 – 100	0.1462				
0 – 187.5	0.1503	–	1910	Hunter	/14/
0 – 254	0.1516				
0 – 333	0.1563				
-253 – 196	0.0205	–	1913	Dewar	/60/
0	0.1442				
50	0.1458				
100	0.1497	–	1941	Luchinskii	/17/
200	0.1578				
300	0.1660				

TABLE 106

Heat capacities of solid, liquid and gaseous titanium
cal/g·atom·deg

Solid Ti				Liquid Ti		Gaseous Ti
T, °K	C_p	T, °K	C_p	T, °K	$C_{p\,(l)}$	$C_{p\,(i)}$*
298	5.98	1200	7.72	2000	8.00	5.86
300	5.98	1300	7.84	2100	8.00	5.99
400	6.36	1400	7.95	2200	8.00	6.13
500	6.62	1500	8.06	2300	8.00	6.27
600	6.84	1600	8.16	2400	8.00	6.41
700	7.02	1700	8.26	2500	8.00	6.55
800	7.18	1800	8.36	2600	8.00	6.70
900	7.33	1900	8.46	2700	8.00	6.84
				2800	8.00	6.99
1000	7.47			2900	8.00	7.13
1100	7.60			3000	8.00	7.28

* The heat capacity of gaseous titanium considered as an ideal monoatomic gas.

The same author /62/ gives the following values for the atomic heat capacity of titanium:
for α-Ti (from 298 to 1150°K):

$$C_p = 5.25 + 2.52 \cdot 10^{-3} T,$$

for β-Ti (from 1150 to 1500°K):

$$C_p = 7.50 \text{ cal/g} \cdot \text{atom} \cdot \text{degree}.$$

Jaeger et al. /63/ derived the following equations for the specific (I) and atomic (II) heat capacity of titanium

$$c_p = 0.08724 + 0.37852 \cdot 10^{-3} t - 0.813165 \cdot 10^{-6} \cdot t^2 + 0.607508 \cdot 10^{-9} \cdot t^3, \quad \text{(I)}$$

$$C_p = 4.1964 + 0.018208 \cdot t - 0.39114 \cdot 10^{-4} \cdot t^2 + 0.29223 \cdot 10^{-7} t^3. \quad \text{(II)}$$

In a later work /64/, these authors give the following equation for the variation in atomic heat capacity with absolute temperature:

$$C_p = 5.9 + 2.96 \cdot 10^{-3}\ T\ (5\%,\ 298 - 750°K).$$

Latent heat of transition of titanium. There are no calorimetric data available on the latent heat of transition of titanium. McQuillan /23/ performed thermodynamic calculations on the variation of the partial pressure of hydrogen with the temperature and on the hydrogen concentration in the system titanium-hydrogen and obtained for the latent heat of the $\alpha \rightleftharpoons \beta$ transition in titanium 678 cal/mole. The accuracy of this value is ±10%.

Kubaschewski and Evans /65/, without giving a reference, propose 350 cal/mole for the heat of $\alpha \rightleftharpoons \beta$ transition in titanium. Kelley /62/ and Stull and Sinke /33/ both give L_{tr} = 950 cal/mole at T_{tr} = 1155°K.

Entropy of transition of titanium. The entropy of the $\alpha \rightleftharpoons \beta$ transition in titanium is ΔS_{tr} = 0.830 cal/g · atom · degree at 1150°K /57/. Other references /23/ give this value as 0.587 cal/g · atom · degree.

Heat of sublimation of titanium. From the data in Table 101 Blocher and Campbell /18/ calculated the heat of sublimation L_{subl} of titanium at the given temperatures from the following equations:

$$R \ln P\ (\text{atm}) = \left(\frac{F_T^0 - H_0}{T}\right)_s - \left(\frac{F_T^0 - H_0}{T}\right)_g = \frac{L_{subl}}{T},$$

where

$$\left(\frac{F_T^\circ - H_0}{T}\right)_s = \frac{1}{T}\int_0^T C_p dT - \int_0^T C_p d \ln T.$$

The free energy of gaseous titanium was determined from spectroscopic data.

The results of the calculation of the heat of sublimation (L_{subl}) of titanium are given in Table 107.

TABLE 107

Heat of sublimation of titanium /18/

T, °K	$\left(\frac{F_T^\circ - H_0}{T}\right)_g$	$\left(\frac{F_T^\circ - H_0}{T}\right)_s$	L^*_{subl}	L^{**}_{subl}
	cal/g · atom · deg		cal/g · atom	
1510	46.282	12.26	111393; 111076	110094
1613	46.637	12.73	111394; 110894	110926
1636	46.713	12.84	110937; 110724	111101
1727	47.005	13.23	111633; 111512	111892
1822	47.294	13.61	110486; 110595	112636

* The values of the first column were obtained from resistance measurements, those of the second from loss in weight.

** The heat of sublimation L_{subl} was calculated from the equation of Carpenter and Reavell /66/.

Of the data of Blocher and Campbell on the sublimation temperature of titanium, Kubaschewski and Evans /65/ consider the following values the most reliable: 111.7± 8.0 kcal/mole at 25° and 106.2± 5.0 kcal/mole at 1730°.

From their data on the vapor pressure of titanium (Table 102) Edwards and co-workers /31/ calculated the heat of sublimation L_{subl} from 1587 to 1764°K. Their results are presented in Table 108.

Rossini and co-workers /32/ consider only one value for the heat of sublimation to be reliable, i.e., L_{subl} = 112 kcal/mole at 298°K. Stull and Sinke /33/ give L_{subl} = 106.5 kcal/g · atom at 1812° and 0.036 mm Hg.

TABLE 108

Heat of sublimation of titanium /31/

T, °K	$-R \ln P$	$-\left(\frac{F_T^\circ - H_0}{T}\right)_s$	$-\left(\frac{F_T^\circ - H_0}{T}\right)_g$	L_{subl} cal/g · atom
	cal/g · atom · deg			
1587	37.1237	12.529	46.551	112923
1624	35.3745	12.688	46.678	112648
1651	34.2826	12.809	46.764	112660
1667	33.7357	12.877	46.815	112814
1675	33.3947	12.910	46.840	112769
1698	32.5005	13.007	46.910	112753
1725	31.4763	13.120	46.995	112721
1764	30.1161	13.280	47.111	112803

Entropy of sublimation of titanium. For the entropy of sublimation, Rossini and co-workers /32/ give ΔS_{subl} = 51.0 cal/g·atom·degree at 1812° and 0.036 mm Hg.

Free energy of sublimation of titanium. For the free energy of sublimation of titanium, Rossini and co-workers /32/ give ΔF°_{subl} = 101 kcal/mole at 298°K.

Latent heat of fusion of titanium. At high temperatures titanium reacts very vigorously with all known refractories, so that the experimental determination of the latent heat of fusion of titanium is very difficult. McQuillan /23/ assumes that the latent heat of fusion is approximately 5 kcal/g · atom. The heat of fusion of titanium is given by Kubaschewski and Evans /65/ as 4.5 ± 0.5 kcal/g · atom, whereas Stull and Sinke /33/ give only 3.7 kcal/mole at 1950°K.

Latent heat of vaporization of titanium. Blocher and Campbell /18/, Carpenter and Mair /53/, and Edwards et al. /31/ determined the latent heat of vaporization as 111.064 ± 0.578, 112.55 ± 0.55, and 112.763 ± 0.153 kcal/g · atom, respectively. The most reliable value for the latent heat of vaporization is that of McQuillan /23/, 112.5 ± 0.3 kcal/g · atom. Stull and Sinke /33/ give the heat of vaporization L_{vap} as 102,500 cal/g · atom at the boiling point of titanium (3550°K).

Heat content and entropy of titanium. The Φ' function.

Heat content of titanium. The data of Jaeger et al. /64/ on the heat content of titanium (Table 109) were found by Kelley /62/ to conform to the following equations:

for α-Ti (accuracy 3%, 298 to 1150°K)

$$H_T - H_{298} = 5.25T + 1.26 \cdot 10^{-3}T^2 - 1677,$$

for β-Ti (accuracy 3%, 1150 to 1500°K)

$$H_T - H_{298} = 7.50T - 1650.$$

TABLE 109

Heat content of titanium /64/

T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom	T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom	T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom
400	625	900	4070	1200	7350
500	1250	1000	4840	1300	8100
600	1920	1100	5630	1400	8850
700	2610	1150(α)	6030	1500	9600
800	3330	1150(β)	6980		

Kothen and Johnston /57/ determined the heat content of titanium from 15 to 298.16°K. Their results are presented in Table 110.

TABLE 110

Heat content of titanium /57/

T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom	T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom	T, °K	Heat content $H_T - H^\circ_{298}$ cal/g·atom
15	0.15	125	229.00	225	727.30
25.0	0.94	150	339.90	250	868.00
50	15.31	175	461.90	275	1012.80
75	50.10	200	591.50	298.16	1149.90
100	133.70				

The heat content of titanium can be calculated from 200 to 817° from the following equation derived by Jaeger et al. /58/.

$$\Delta H_T = 0.08724t + 0.18926 \cdot 10^{-3}t^2 -$$
$$- 0.271055 \cdot 10^{-6}t^3 + 0.151877 \cdot 10^{-9}t^4.$$

Table 111 shows the heat content of solid, liquid, and gaseous titanium, according to Stull and Sinke /33/. The second column of this table contains the heat content of solid, liquid, and gaseous titanium, the third column that of gaseous titanium, considered as an ideal monoatomic gas.

Entropy of titanium. Kothen and Johnston /57/ determined the entropy of titanium from 15 to 298°K. Their results are presented in Table 112.

TABLE 111

Heat contents of solid, liquid, and gaseous titanium /33/

T, °K	Heat content		T, °K	Heat content	
	$H_T - H^\circ_{298}$ cal/g · atom	$H_T - H^\circ_{298}$ cal/g · atom		$H_T - H^\circ_{298}$ cal/g · atom	$H_T - H^\circ_{298}$ cal/g · atom
298	0	0	1700	11290	7370
300	11	11	1800	12130	7926
400	629	577	1900	12970	8494
500	1280	1119	2000	17500	9074
600	1960	1648	2100	18300	9666
700	2640	2168	2200	19100	10273
800	3355	2683	2300	19900	10893
900	4080	3194	2400	20700	11527
1000	4820	3704	2500	21500	12175
1100	5575	4214	2600	22300	12837
1200	7290	4726	2700	23100	13514
1300	8070	5241	2800	23900	14206
1400	8860	5762	2900	24700	14912
1500	9660	6289	3000	25500	15633
1600	10470	6825			

TABLE 112

Entropy of solid titanium /57/

T, °K	S°_T cal/g·at.deg	T, °K	S°_T cal/g·at·deg	T, °K	S°_T cal/g·at·deg
15	0.013	125	2.811	225	5.735
25	0.054	150	3.652	250	6.328
50	0.414	175	4.403	275	6.879
75	1.123	200	5.095	298.16	7.334
100	1.963				

The entropy of titanium, as determined by various authors, is given in Table 113.

TABLE 113

Entropy of titanium, cal/g · atom · deg

S°_{298}	Year	Author	Reference
10.62	1921	Latimer	/67/
6.6 ± 0.4	1917	Lewis, Gibson	/68/
6.5± 0.0	1922	Lewis, Gibson, Latimer	/69/
6.3	1923	Eastman	/70/

Kelley /71/ calculated the entropy of solid titanium from its heat capacity and found S^0_{298} = 7.24 ± 0.05 cal/g · atom · degree.

Kubaschewski and Evans /65/, referring to Kelley's work, give S^0_{298} = 7.2 ± 0.4 cal/g · atom · degree. Rossini and co-workers /32/ consider the most reliable value to be 7.24 cal/g · atom · degree.

The entropy of gaseous titanium was calculated by Bacher and Goudsmit /72/ as $S^0_{298} = 43.07 \pm 0.1$ cal/g · atom · degree. Kelley /71/ and Rossini et al. /32/ give $S^0_{298} = 43.08 \pm 0.01$ cal/g · atom · degree and $S^0_{298} = 43.069$ cal/g · atom · degree, respectively.

Kelley /71/ quotes the data of Jaeger et al. /64/ on entropies from 400 to 1500°K (Table 114).

TABLE 114

Entropy of solid titanium /71/ in cal/g · atom · deg

T, °K	$S^\circ_T - S^\circ_{298}$	T, °K	$S^\circ_T - S^\circ_{298}$	T, °K	$S^\circ_T - S^\circ_{298}$
400	1.80	900	7.31	1200	10.38
500	3.20	1000	8.12	1300	10.98
600	4.42	1100	8.87	1400	11.53
700	5.48	1150 (α)	9.23	1500	12.05
800	6.44	1150 (β)	10.06		

Table 115 contains entropies of solid, liquid, and gaseous titanium, according to Stull and Sinke /33/. The second column presents entropies of liquid, solid, and gaseous titanium, the third column the entropy of titanium, considered as ideal monoatomic gas.

TABLE 115

Entropies of solid, liquid and gaseous titanium /33/

T, °K	Entropy		T, °K	Entropy	
	S°_T cal/deg·g·at.	S°_T cal/deg·g·at.		S°_T cal/deg·g·at.	S°_T cal/deg·g·at.
	Solid titanium α		1500	19.44	51.63
			1600	19.96	51.98
298	7.33	43.07	1700	20.46	52.31
300	7.37	43.10	1800	20.94	52.63
400	9.15	44.74	1900	21.39	52.93
500	10.60	45.95			
600	11.82	46.91		Gaseous titanium	
700	12.89	47.71			
800	13.84	48.40	2000	23.71	53.23
900	14.70	49.00	2100	24.10	53.52
1000	15.48	49.54	2200	24.47	53.80
1100	16.19	50.03	2300	24.83	54.08
			2400	25.17	54.35
	Solid titanium β		2500	25.50	54.61
			2600	25.81	54.87
1200	17.68	50.47	2700	26.11	55.13
1300	18.30	50.88	2800	26.40	55.38
1400	18.89	51.27	2900	26.68	55.63
			3000	26.96	55.87

Free energy function of titanium. Kothen and Johnston /57/ calculated the function $\Phi' = -\frac{F^0_T - H^0_0}{T}$ at low temperatures up to 298.16°K. Their results are presented in Table 116.

Values of the function $\Phi'' = -\frac{F^0_T - H^0_{298}}{T}$ for solid, liquid, and gaseous titanium are given in the second column of Table 117. The third column of this

table contains values for the Φ'' of titanium considered as an ideal monoatomic gas (Stull and Sinke /33/).

TABLE 116

Φ'' for titanium /57/

T, °K	Φ'' cal/g-at-deg	T, °K	Φ'' cal/g-at-deg	T, °K	Φ'' cal/g-at-deg
15	0.003	125	0.979	225	2.502
25	0.017	150	1.383	250	2.856
50	0.108	175	1.764	275	3.196
75	0.322	200	2.137	298.16	3.478
106	0.626				

TABLE 117

$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$ for solid and liquid titanium /33/

T, °K	$-\frac{F_T^\circ - H_0^\circ}{T}$ cal/g-at-deg	$\frac{F_T^\circ - H_0^\circ}{T}$ cal/g-at-deg	T, °K	$-\frac{F_T^\circ - H_0^\circ}{T}$ cal/g-at-deg	$\frac{F_T^\circ - H_0^\circ}{T}$ cal/g-at-deg
Solid titanium α			Solid titanium β		
298	7.33	43.07	1500	13.00	47.44
300	7.34	43.07	1600	13.42	47.72
400	7.58	43.30	1700	13.82	47.98
500	8.04	43.72	1800	14.21	48.23
600	8.57	44.17	1900	14.57	48.46
700	9.12	44.62	Liquid titanium		
800	9.65	45.05	2000	14.96	48.70
900	10.17	45.46	2100	15.39	48.92
1000	10.66	45.84	2200	15.79	49.14
1100	11.13	46.20	2300	16.18	49.35
Solid titanium β			2400	16.55	49.55
1200	11.61	46.54	2500	16.90	49.74
1300	12.10	46.85	2600	17.24	49.94
1400	12.57	47.16	2700	17.56	50.13
			2800	17.87	50.31
			2900	18.17	50.49
			3000	18.46	50.66

15. OXIDES OF TITANIUM

The following oxides of titanium are known: TiO, Ti_3O_4, Ti_2O_3, Ti_3O_5, TiO_2, and TiO_3.

Titanium monoxide TiO (M = 63.9)

Crystal structure of TiO. As it was reported by Ehrlich /73/, and later confirmed by other authors /2/, the compound TiO has a

face-centered cubic lattice of the NaCl type. The unit cell parameter of TiO is 4.24 Å. /75/. According to Ehrlich /73/, the crystal lattice parameter of stoichiometric TiO is 4.165 Å. Grove et al. /82/ studied the solid phase of TiO by X-ray methods and came to the conclusion that there are no substantial changes in structure up to the melting point.

Density of TiO. Bräkken /76/ and Dawihl and Schröter /77/ give the density of TiO as 5.53 g/cm^3 and 4.93 g/cm^3, respectively.

$\alpha \rightleftharpoons \beta$ transition temperature in TiO. Naylor reports /78/ that the $\alpha \rightleftharpoons \beta$ temperature transition in TiO (more correctly $TiO_{0.7-1.25}$) takes place at 1264°K. According to Kubaschewski and Hopkins /79/, the transition temperature is 990°. Kubaschewski and Evans /65/ consider the most reliable value to be 991°. The same value is given by Rossini et al. /32/.

Melting point of TiO. Pirani and Alterthum /80/ determined the melting point of TiO as 1750°. Bumps, Kessler, and Hansen /81/ (1952) found that the solid phase of TiO is subject to a peritectic reaction and decomposes at 2010°K to give α-titanium and a liquid phase. Kubaschewski and Evans /65/ give the melting point of TiO as 2020°K.

Vapor pressure of TiO. Grove et al. /82/ studied the vapor pressure of TiO by the Knudsen effusion method. The results of these experiments obey the following equation for the vapor pressure of TiO:

$$\log P = -\frac{29{,}421}{T} - 0.583 \cdot 10^{-3} T + 10.43.$$

According to Gilles and Wheatley /83/, the total pressure of the gaseous phase in equilibrium with the [solid phase of] TiO is 10^{-3} atm at 2275± 50°K, and 1 atm at 2970± 100°K.

Heat capacity of TiO. The molar heat capacities of solid TiO at low temperatures are given below according to Kelley /62/.

Temperature, °K	10	25	50	100	150	200	298.16
Molar heat capacity cal/deg·mole	(0.00)*	(0.09)*	0.65	3.05	5.47	7.34	9.55

Kelley /62/, using the data of Naylor /78/, has calculated the following equations for the molar heat capacity of titanium monoxide:
for α-TiO (accuracy 1.5%, 298 to 1264°K)

$$C_p = 10.57 + 3.60 \cdot 10^{-3} T - 1.86 \cdot 10^{5} T^{-2},$$

and for β-TiO (accuracy 1%, 1264 to 1800°K)

$$C_p = 11.85 + 3.00 \cdot 10^{-3} T.$$

The heat capacity of TiO under standard conditions is $C_{P_{298}} = 9.55$ cal/mole·degree, according to /32/.

Heat of $\alpha \rightleftharpoons \beta$ transition in TiO. Naylor /78/ determined the heat of the $\alpha \rightleftharpoons \beta$ transition in TiO as 0.82 ± 0.2 kcal/mole at 1264°K. The same value is given by Rossini et al. /32/ and also by Kelley /13/.

Entropy of transition of TiO. The entropy of transition of TiO as given by Kelley /62/ and Rossini et al. /32/ is ΔS = 0.65 cal/mole·degree at 1264°K.

Heat of fusion of TiO. Kubaschewski and Evans /65/ give the heat of fusion of TiO as 14.0 ± 1.5 kcal/mole.

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* Extrapolated.

Heat of sublimation of TiO. According to Gilles and Wheatley /83/, the heat of sublimation of solid TiO is given by L^0_{subl} = 135± 1 kcal/mole at 298°K. Grove and co-workers /82/ give 134.6 kcal/mole. Using a mass-spectrometric technique, Berkowitz et al. /84/ obtained L^0_{subl} = 139 kcal/mole at 298°K for the sublimation process TiO (s) ⇌ TiO (g).

Energy of dissociation of TiO. The energy of dissociation of titanium monoxide into the atoms according to the reaction TiO (g) = Ti (g) + O at 0°K was calculated by extrapolation and is 160 ± ?* kcal/mole, according to Gilles and Wheatley /83/.

Heat content of TiO. The data of Naylor /78/ on the heat content of TiO are presented in Table 118. These data were found by Kelley /62/ to conform to the following equation:
for TiO (α) (accuracy 1%, 298 to 1264°K)

$$H_T - H^\circ_{298} = 10.56T + 1.8 \cdot 10^{-3}T^2 + 1.86 \cdot 10^5 T^{-1} - 3935,$$

and for TiO (β) (accuracy 0.5%, 1264 to 1800°K)

$$H_T - H^\circ_{298} = 11.85T + 1.50 \cdot 10^{-3}T^2 - 4100.$$

The heat content ΔH** of titanium monoxide was calculated by Samsonov /93/ from data on the reduction of titanium dioxide with carbon (TiO_2 + C = TiO + CO) and equation $\log K_p = \log P_{CO} = 4.574T \cdot (T\Delta S - \Delta H)$. The result of the calculation was 139.37 kcal/mole, valid from 960 to 1233°. This value is rather close to the experimental values obtained by other authors.

TABLE 118

Heat content of TiO, cal/mole /78/

T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$
400	1080	900	7230	1264(β)	13270
500	2220	1000	8600	1300	13840
600	3410	1100	10020	1400	15430
700	4640	1200	11490	1500	17050
800	5910	1264(α)	12450		

Entropy of TiO. Kelley /62/ gives the data of Naylor /78/ on the entropy of TiO from 400 to 1500°K (Table 119).

TABLE 119

Entropy of TiO /78/, kcal/mole · deg

T, °K	$S^0_T - S^0_{298}$	T, °K	$S^0_T - S^0_{298}$	T, °K	$S^0_T - S^0_{298}$
400	3.11	900	12.96	1264 (β)	18.46
500	5.65	1000	14.40	1300	18.90
600	7.82	1100	15.75	1400	20.08
700	9.71	1200	17.03	1500	21.20
800	11.47	1264 (α)	17.81		

* [Figure missing in original text.]

** [Heat of formation may be meant.]

Kelley /71/ used the data of Shomate /85/ on the heat capacity of titanium monoxide at low temperatures to calculate the entropy of solid TiO. He obtained the following results: S^0_{52} = 0.25 (extrapolated), $S^0_{298} - S^0_{52}$ = 8.06 (experimental), and S^0_{298} = 8.31 ± 0.04 cal/degree · mole.

Kelley /71/ used data on molar constants /86/ and spectroscopic results /87/ to calculate the entropy of gaseous titanium monoxide. He obtained S^0_{298} = 55.80 ± 0.10 cal/mole · degree for TiO (g). Kubaschewski and Evans /65/ quote the data of Shomate /85/ on the entropy of solid TiO and consider 8.3 ± 0.1 cal/mole · degree to be the most reliable value; the same value is given by Rossini et al. /32/.

Heat of formation of TiO. Humphrey /88/ found that the heat of formation of TiO (g) at 0° is given by ΔH^0 = −123.9 kcal/mole. Brewer /74/, with reference to Humphrey /88/, gives ΔH^0_{298} = 123.9 ± 0.3 kcal/mole. Kubaschewski and Evans /65/ give ΔH^0_{298} = −135.0 ± 10.0 kcal/mole.

The heat of formation of gaseous TiO is given as ΔH^0_{298} = 43 kcal/mole. The same value is given by Rossini and co-workers /32/.

Entropy of formation of TiO. For the entropy of formation of solid TiO, Brewer /74/ gives ΔS^0_{298} = −22.8 cal/mole · degree.

Free energy of formation of TiO. The free energy of the formation of TiO was determined by Humphrey /88/ as −116.92 kcal/mole at 0°. Brewer /74/ gives ΔF^0_{298} = −117.1 kcal/mole.

For the free energy of formation of solid TiO, Kubaschewski /89/ gives the following equation:

$$\Delta F^\circ_T = -135{,}600 - 3.58T \log T + 34.17T,$$

valid from 298 to 2000°K. Its accuracy is ±8 kcal/mole.

Titanium (II, III oxide) Ti_3O_4 (M = 207.70)

Titanium (II, III) oxide Ti_3O_4 is unstable /79/. The metastability of Ti_3O_4, which is similar to that of V_3O_4, was pointed out by Chretien and Wyss /90/.

Titanium sesquioxide Ti_2O_3 (M = 149.8)

Crystal structure of Ti_2O_3. Ehrlich /73/ found that Ti_2O_3 has a hexagonal crystal structure of the corundum type with the following lattice parameters: a = 5.15 Å, c = 13.61 Å, and c/a = 2.64.

According to Grove et al. /82/, no appreciable structural changes occur in Ti_2O_3 up to its melting point.

Temperature of the $\alpha \rightleftharpoons \beta$ transition in Ti_2O_3. Fox and Leriers /91/ report that the $\alpha \rightleftharpoons \beta$ transition in Ti_2O_3 takes place at 473°K. Naylor /78/, reexamined the data of Fox and Leriers /91/ and confirmed this temperature. The same value is given by Kubaschewski and Evans /65/ and by Rossini and co-workers /32/.

Melting point of Ti_2O_3. Brewer /74/, Kubaschewski and Evans /65/ give the melting point of Ti_2O_3 as 2400°K.

Vapor pressure of Ti_2O_3. Vaporization of Ti_2O_3 was investigated by Grove et al. /82/, using the Knudsen effusion method. The authors

found that Ti_2O_3 decomposes into TiO (g) + TiO_2 (g). The heat change accompanying this decomposition is given by ΔH_0^0 = 296.0 kcal/mole. From the data of these authors the following equation was derived:

$$\log P_{TiO} P_{TiO_2} = -\frac{64,700}{T} - 1.26 \cdot 10^{-3} T + 21.65.$$

Mott /51/ determined the boiling point of Ti_2O_3 as 3300°K. Brewer /74/ states that at 3300 ± 300°K the total pressure of the gaseous products of Ti_2O_3 in equilibrium with the solid phase is 1 atm.

Heat capacity of Ti_2O_3. Data on the heat capacity of solid Ti_2O_3 at low temperatures are given by Kelley /71/.

Temperature, °K	10	25	50	100	150	200	296.16
Molar heat capacity, cal/mole·deg	(0.01)*	(0.17)*	1.26	6.30	12.30	17.26	24.27

According to Naylor /78/, the molar heat capacity of Ti_2O_3 is given by the following equations:

for Ti_2O_3 (α) (accuracy 2%, 298 to 473°K)

$$C_p = 7.31 + 53.52 \cdot 10^{-3} T;$$

for Ti_2O_3 (β) (accuracy 1%, 473 to 1800°K)

$$C_p = 34.68 + 1.30 \cdot 10^{-3} T - 10.20 \cdot 10^5 \cdot T^{-2}.$$

Rossini and co-workers /32/ give the C_p for Ti_2O_3 as 23.27 cal/mole·deg. at 298°K.

Heat of transition of Ti_2O_3. Naylor /78/ determined the heat of transition of Ti_2O_3 and found L_{trans} = 215 cal/mole at 473°K. Kubaschewski and Evans /65/, referring to the work of Naylor /78/, and also Rossini and co-workers /32/, give L_{trans} = 0.22 ± 0.05 kcal/mole.

Entropy of transition of Ti_2O_3. According to Naylor /78/, the entropy of the $\alpha \rightleftharpoons \beta$ transition is given by ΔS = 0.450 cal/mole · degree at 473°K. Rossini /32/ and co-workers give ΔS_{trans} = 0.46 at 473°K.

Heat content of Ti_2O_3. The heat content of Ti_2O_3, according to Naylor /78/, is given in Table 120. According to Kelley /71/, these values fit the following equations:

for Ti_2O_3 (α) (accuracy 2%, 298 to 473°K)

$$H_T^\circ - H_{298}^\circ = 7.31T + 26.76 \cdot 10^{-3} T^2 - 4558;$$

for Ti_2O_3 (β) (accuracy 0.5%, 473 to 1800°K)

$$H_T^\circ - H_{298}^\circ = 34.68T + 0.65 \cdot 10^{-3} T^2 + 10.20 \cdot 10^5 T^{-1} - 13,605.$$

TABLE 120

Heat content of Ti_2O_3, cal/mole /78/

T, °K	$H_T - H_{298}^\circ$	T, °K	$H_T - H_{298}^\circ$	T, °K	$H_T - H_{298}^\circ$
400	2610	800	15830	1400	36950
473 (α)	4885	900	19270	1500	40560
473 (β)	5100	1000	22740	1600	44180
500	5935	1100	26260	1700	47830
600	9140	1200	29800	1800	51490
700	12440	1300	33360		

* Extrapolated.

Entropy of Ti_2O_3. The data of Naylor /78/ from 400 to 1800°K are presented in Table 121.

TABLE 121

Entropy of Ti_2O_3, cal/mole · deg /78/

T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$
400	7.49	800	30.31	1400	49.96
473 (α)	12.70	900	34.36	1500	52.46
473 (β)	13.15	1000	38.02	1600	54.79
500	14.87	1100	41.38	1700	57.00
600	20.71	1200	44.46	1800	59.10
700	25.79	1300	47.30		

From the heat capacity data of Shomate /85/ for solid Ti_2O_3, from 53 to 297°K, the author obtained $S^0_{298} = 18.18 \pm 0.09$ cal/mole · degree (the sum of the entropies $S^0_{52} = 0.50$ (extrapolated) and $S^0_{298} - S^0_{52} = 18.33$ cal/mole · degree (experimental)). Kubaschewski and Evans /65/, referring to the work of Shomate /85/, give $S^0_{298} = 18.83 \pm 0.2$ cal/mole · degree. The same value is also given by Rossini and co-workers /32/.

Heat of formation of Ti_2O_3. According to Nasu /92/, the heat of formation of Ti_2O_3 for the reaction $2Ti + \frac{3}{2}O_2 = Ti_2O_3$ -388.070 kcal/mole. Humphrey /88/ gives $\Delta H^0_{298} = -363.0 \pm 0.3$ kcal/mole.

The following values for the heat of formation of Ti_2O_3 are given by various authors: $\Delta H^0_{298} = -375.5 \pm 9.0$ kcal/mole (Kubaschewski and Evans /65/), $\Delta H^0_{298} = -363.0 \pm 0.3$ kcal/mole (Brewer /74/), $\Delta H^0_{298} = -367$ kcal/mole (Rossini et al. /32/).

Entropy of formation of Ti_2O_3. Brewer /74/ gives $\Delta S^0_{298} =$ 67.8 cal/mole · degree.

Free energy of formation of Ti_2O_3. According to Humphrey /88/, the free energy of formation of Ti_2O_3, according to $2Ti(s) + 3/2O_2 = Ti_2O_3$ is given by $\Delta F^0 = -342.3$ kcal/mole at 0°. Brewer /74/ gives $\Delta F^0_{298} = -342.6$ kcal/mole, Rossini et al. /32/ $\Delta F^0_{298} = -346$ kcal/mole.

Kubaschewski and Evans /65/ give the following equation for the free energy of formation of solid Ti_2O_3:

$$\Delta F^\circ_T = -377{,}300 - 14.78T \log T + 110.0T \text{ cal/mole.}$$

The accuracy of this equation is ±15 kcal/mole.

Titanium oxide Ti_3O_5 (M = 223.7)

Crystal structure of Ti_3O_5. Ti_3O_5 has an orthorhombic structure according to Rusakov and Zhdanov /94/.

Heat of transition of Ti_3O_5. According to Naylor /78/, the allotropic transition of Ti_3O_5 from the α- to the β-phase occurs at 450°K. The same temperature is given by Rossini et al. /32/.

Heat capacity of Ti_3O_5. The molar heat capacity of solid Ti_3O_5 at low temperatures is given below /71/:

Temperature, °K	10	25	50	100	150	200	298.16
Molar heat capacity, cal/mole·deg.	(0.02)*	(0.34)*	2.43	11.00	20.10	27.35	37.00

Rossini and co-workers /32/ give C_P = 37.00 cal/mole · degree at 298°K.

According to Naylor /78/, the molar heat capacity of Ti_3O_5 on the absolute temperature is described by the following equations:
for Ti_3O_5 (α) (accuracy 5%, 298 to 450°K)

$$C_p = 35.47 + 29.50 \cdot 10^{-3} T,$$

and for Ti_3O_5 (β) (accuracy 1%, 450 to 1400°K)

$$C_p = 41.60 + 8.0 \cdot 10^{-3} T.$$

Heat of transition of Ti_3O_5. Naylor /78/, Rossini and co-workers /32/ give the heat of the $\alpha \rightleftharpoons \beta$ transformation in Ti_3O_5 as 2.24 ± 0.2 kcal/mole.

Entropy of transition of Ti_3O_5. According to Naylor /78/, the entropy of the $\alpha \rightleftharpoons \beta$ transition is given by S_{trans} = 4.98 cal/mole · degree. Rossini and co-workers /32/ give 4.9 cal/mole · degree.

Heat content of Ti_3O_5. The data of Naylor /78/ from 400 to 1400°K are presented in Table 122 and are found to obey the following equations:
for Ti_3O_5 (α) (accuracy 4%, 298 to 450°K)

$$H_T - H^\circ_{298} = 35.47T + 14.75 \cdot 10^{-3} T^2 - 11{,}887;$$

and for Ti_3O_5 (β) (accuracy 1%, 450 to 1400°K)

$$H_T - H^\circ_{298} = 41.60T + 4.00 \cdot 10^{-3} T^2 - 10{,}230.$$

TABLE 122

Heat content of Ti_3O_5 /78/, cal/mole

T, °K	$H_T - H^0_{298}$	T, °K	$H_T - H^0_{298}$	T, °K	$H_T - H^0_{298}$
400	4660	700	20880	1100	40370
450 (α)	7060	800	25550	1200	45510
450 (β)	9300	900	30290	1300	50660
500	11570	1000	35230	1400	55810
600	16220				

The entropy of Ti_3O_5 from 400 and 1400°K, according to Naylor /78/, is given in Table 123.

TABLE 123

Entropy of Ti_3O_5 /78/, cal/mole · deg.

T, °K	$S^0_T - S^0_{298}$	T, °K	$S^0_T - S^0_{298}$	T, °K	$S^0_T - S^0_{298}$
400	13.43	700	44.50	1100	66.42
450 (α)	19.08	800	50.74	1200	70.89
450 (β)	24.06	900	56.31	1300	75.01
500	28.85	1000	61.52	1400	78.83
600	37.32				

From the heat capacity data of Shomate /85/ Kelley calculated the entropy of Ti_3O_5 as S^0_{298} = 30.9 ± 0.2 cal/mole · degree. He obtained this

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* Extrapolated.

value by addition of the following entropies: S_{52} = 0.97 cal/mole · degree (extrapolated result) and $S^0_{298} - S^0_{52}$ = 29.95 cal/mole · degree (experimental).

Kubaschewski and Evans /65/, referring to the work of Shomate /85/, give S^0_{298} = 30.9 ± 0.3 cal/mole · degree. Rossini and co-workers /32/ give S^0_{298} = 30.92 cal/mole · degree.

Heat of formation of Ti_3O_5. Humphrey /88/ measured the heat of formation of Ti_3O_5 at 0° and found ΔH° = −586.9 kcal/mole. Brewer /74/, referring to the work of Humphrey /88/, gives ΔH^0_{298} = −587.0 ± 0.5 kcal/mole, Rossini and co-workers /32/ give ΔH^0_{298} = −584 kcal/mole.

Entropy of formation of Ti_3O_5. Brewer /74/ gives ΔS^0_{298} = −63.5 cal/mole · degree.

Free energy of formation of Ti_3O_5. According to Humphrey /88/, free energy of formation of Ti_3O_5 is given by ΔF^0_{298} = −553.1 kcal/mole. Brewer /74/ gives ΔF^0_{298} = −553.0 kcal/mole, Rossini et al. /32/ give ΔF^0_{298} = −550 kcal/mole.

Titanium dioxide TiO_2 (M = 79.9)

Titanium dioxide TiO_2 exists in rutile, anatase, and brookite forms.

Crystal structure of TiO_2. Rutile has a tetragonal crystal structure with two molecules per cell. The lattice parameters of rutile are a = 4.58 Å, c = 2.95 Å /3/.

The most recent determination of the lattice parameters of rutile is that of Legrand and Delville /95/: a = 4.584 ± 0.002 Å; c = 2.953 ± 0.001 Å; c/a = 0.644.

Grove et al. /82/ report that the structure of rutile does not change appreciably up to its melting point.

Anatase is similar to rutile and has a tetragonal crystal structure whose lattice parameters are: a = 3.78 Å, and c = 9.49 Å (Wyckoff /96/).

Brookite, has an orthorhombic crystal structure.

Density of TiO_2. Densities of titanium dioxide as determined by various authors are given in Table 124.

TABLE 124

Density of TiO_2

Density g/cm^3	Modification	Year	Author	Reference
4.21	Annealed rutile	1902	Geisow	/97/
4.24	Synthesized rutile	1934	Rheinboldt, Wisfeld	/98/
4.19—4.215	Synthesized TiO_2	1941	Luchinskii	/17/
4.1	Molten TiO_2			
3.904 ± 0.002	Synthesized anatase	1956	Lietz	/99/
4.150 ± 0.002	Synthesized anatase			

Molar volume of TiO_2. The molar volume of titanium dioxide as determined by various authors is given in Table 125.

Coefficient of linear expansion of TiO_2. Maximum and minimum values of the coefficient of linear thermal expansion α are $14.4938 \cdot 10^{-6}$ and $8.1900 \cdot 10^{-6}$ degree^{-1}, respectively (Slavinskii /102/).

Transition temperature of TiO_2. The transition temperature of TiO_2 was investigated by Hautefeuille /103/. He found that a mixture of potassium titanate and KCl, heated in an atmosphere of gaseous HCl and air, produces anatase at 700 to 800°, brookite at 800 to 1040°, and rutile above 1040°. Junker /104/ showed that rutile is converted into brookite at about 1300°.

TABLE 125

Molar volume of TiO_2

Molar volume	Year	Author	Reference
18.85	1903	Stefanovic	/100/
20.65*	1908	Gollas	/101/
18.80**	1955	Kubaschewski, Hopkins	/79/
19.30*			
19.8 – 20.5†			

* Anatase
** Rutile
† Brookite

Brewer /74/ reports that anatase and brookite are thermodynamically unstable, but may be stabilized by addition of admixtures. The rate of conversion of both modifications to rutile is slow. It can, however, be accelerated at temperatures above 700 to 1100°K by use of a flux. The transition temperature of α and β anatase is 642° /32/.

Melting point of TiO_2. The melting point of TiO_2, as given by various authors, is shown in Table 126.

TABLE 126

Melting point of TiO_2

Melting point, °C	Titanium dioxide	Year	Author	Reference
1640	Rutile	1913	Ruff et al.	/105/
1640	"	1913	Fletcher	/106/
1857	Partially reduced	1925	Friedrich, Sittig	/107/
~1800	Synthesized	1936	Junker	/104/
1825	—	1933	Bunting	/108/
1855 ± 20	—	1937	Wartenberg et al.	/109/

The most reliable values for the melting point of TiO_2 rutile are 1860° /79/ and 1850° /65/.

Boiling point of TiO_2. According to Mott /51/ the boiling point of TiO_2 is approximately 3000°. The same temperature is given by Kubaschewski and Evans /65/. Brewer /74/ gives 3200 ± 300°K. At this temperature the total pressure of the gaseous products of disproportionation of TiO_2 is 1 atm.

Dissociation temperature of TiO_2. The dissociation temperature of TiO_2 was investigated by Born /110/. He showed that TiO_2 dissociates into oxygen and titanium, both at 2000° and 1 atm and 3000° and 10^{-3} atm.

Junker /104/ showed that dissociation of TiO_2 occurs at 2230° with formation of lower oxides.

Vapor pressure of TiO_2. The following equation for the sublimation pressure of TiO_2 is based on the experimental work of Grove et al. /82/:

$$\log P = -\frac{30,361}{T} - 0.492 \cdot 10^{-3}T + 11.19.$$

where T is the temperature in degrees absolute.

Heat capacity of TiO_2. The heat capacities of both rutile and anatase at low temperatures are given below /71/:

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity of rutile, cal/mole·deg	(0.02)*	(0.22)*	1.45	4.43	7.57	10.05	13.16
Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity of anatase, cal/mole·deg	(0.01)*	(0.18)*	1.17	4.59	7.62	10.00	13.22

Kelley /62/ gives the following equations for the heat capacities of the two allotropes:
for rutile (298 to 1800°K)

$$C_p = 17.97 + 0.28 \cdot 10^{-3}T - 4.35 \cdot 10^{5}T^{-2},$$

for anatase (298 to 1300°K)

$$C_p = 17.83 + 0.50 \cdot 10^{-3}T - 4.23 \cdot 10^{5}T^{-2}.$$

These equations were derived from the data of Naylor /78/. Kubaschewski and Evans /65/, referring to the work of /78/, give the following two equations:
for rutile (298 to 1800°K)

$$C_p = 17.21 + 1.08 \cdot 10^{-3}T - 3.59 \cdot 10^{5}T^{-2},$$

and for anatase (298 to 1300°K)

$$C_p = 17.14 + 0.98 \cdot 10^{-3}T - 3.50 \cdot 10^{5}T^{-2}.$$

Kelley /61/ gives the following equation for molar heat capacity of TiO_2 from 298 to 1300°K:

$$C_p = 11.81 + 7.54 \cdot 10^{-3}T - 0.419 \cdot 10^{5}T^{-2}.$$

Lietz /99/ later determined experimentally the molar heat capacities of rutile and anatase. His data for synthetic rutile from 304 to 1009° and synthetic anatase from 307 to 728° fit the following equations:
for rutile

$$C_p = 13.43 + 10.24 \cdot 10^{-3}t - 6.27 \cdot 10^{-6}t^2,$$

and for anatase

$$C_p = 13.52 + 1.28 \cdot 10^{-3}t - 12.3 \cdot 10^{-6}t^2.$$

Rossini et al. /32/ give $C_{P_{298}} = 13.16$ and $C_{P_{298}} = 13.22$ cal/mole · degree for rutile and anatase, respectively.

Heat of transition of TiO_2. Rossini and co-workers /32/ give the heat of the $\alpha \rightleftharpoons \beta$ transition in anatase as $L_{trans} = 0.3$ kcal/mole at 642°.

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* Extrapolated.

Entropy of transition of TiO_2. The entropy of transition of anatase at 642° is given by $\Delta S_{trans} = 0.3$ cal/mole · degree /32/.

Heat of fusion of TiO_2. From a study of the $TiO_2 - Al_2O_3$ system, Bunting /108/ calculated a heat of fusion of 11,400 cal/mole.

This value however is not accurate. Kubaschewski and Evans /65/ give $L_{fus} = 15.5 \pm 2.5$ kcal/mole.

Heat of sublimation of TiO_2. Grove et al. /82/ studied the vaporization of TiO_2 by the Knudsen effusion method and found $L_{subl} = 138.9$ kcal/mole at 0° for TiO_2 (s) → TiO_2 (g).

$L_{subl} = 146.0$ kcal/mole at 298°K was obtained by Berkowitz et al. /84/, using mass-spectrometric methods.

Heat content of TiO_2. Data of Naylor /78/ on the heat content of rutile and anatase are presented in Tables 127 and 128.

TABLE 127

Heat content of rutile TiO_2 cal/mole, /78/

T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$
400	1540	900	9900	1400	18820
500	3100	1000	11650	1500	20660
600	4735	1100	13420	1600	22540
700	6440	1200	15200	1700	24440
800	8160	1300	17000	1800	26340

TABLE 128

Heat content of anatase TiO_2 cal/mole, /78/

T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$
400	1540	800	8170	1100	13530
500	3100	900	9930	1200	15350
600	4735	1000	11720	1300	17180
700	6440				

The data of Tables 127 and 128 obey the following equations: for rutile (accuracy 1%, 400 to 1800°K)

$$H_T - H^\circ_{298} = 17.97T + 0.14 \cdot 10^{-3}T^2 + 4.35 \cdot 10^5 T^{-1} - 6829,$$

and for anatase (accuracy 1%, 400 to 1300°K)

$$H_T - H^\circ_{298} = 17.83T + 0.25 \cdot 10^{-3}T^2 + 4.23 \cdot 10^5 T^{-1} - 6757.$$

Entropy of TiO_2. The entropies of both allotropic forms of TiO_2 are presented in Tables 129 and 130.

The entropy of rutile TiO_2 was calculated from heat capacity data obtained by McDonald and Seltz /111/. They gave $S^0_{298} = 12.4 \pm 0.2$ cal/mole · degree. Shomate /112/ calculated the entropy of rutile from his own heat capacity data. He gave $S^0_{298} = 12.01 \pm 0.07$ cal/mole · degree, which he obtained by summing $S^0_{52} = 0.60$ (extrapolated result) and $S^0_{298} - S^0_{52} = 11.41$ (direct measurements). The same author /112/ gave the entropy of anatase as $S^0_{298} = 11.93$ cal/mole·degree, which he obtained by summing $S^0_{52} = 0.50$ (extrapolated result) and $S^0_{298} - S^0_{52} = 11.43$ (direct measurement).

Kubaschewski and Evans /65/, referring to the work of Shomate /85/, give S^0_{298} = 12.0± 0.05 for rutile and S^0_{298} = 11.93± 0.1 cal/mole · degree for anatase. Rossini and co-workers /32/ give the same values. Kelley /113/ gives S^0_{298} = 11.9 cal/mole · degree for anatase.

TABLE 129

Entropy of rutile TiO_2 cal/mole · deg /62/

T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$
400	4.43	900	17.86	1400	25.73
500	7.91	1000	19.70	1500	27.00
600	10.89	1100	21.39	1600	28.21
700	13.51	1200	22.94	1700	29.36
800	15.81	1300	24.38	1800	30.45

TABLE 130

Entropy of anatase TiO_2 cal/mole · deg /62/

T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$
400	4.43	800	15.82	1100	21.51
500	7.91	900	17.89	1200	23.09
600	10.89	1000	19.78	1300	24.55
700	13.52				

The heat of formation of TiO_2 is presented in Table 131.

TABLE 131

Heat of formation of TiO_2, kcal/mole

Heat of formation $-\Delta H^\circ_{298}$	Method	Year	Author	Reference
215.6	Heating titanium with sodium peroxide	1908	Mixter	/114/
218.4	Oxidation of finely ground titanium powder with oxygen	1909	Mixter	/115/
217.4	—	1928	Berkenheim	/116/
218.7 ± 0.3	Combustion of titanium with paraffin oil	1931	Roth, Becker	/117/
220.7 ± 0.1	—	1931	Sieverts, Gotta	/118/
225.3 ± 0.3	Combustion of titanium powder in a current of oxygen at 1250°	1934	Neumann et al.	/119/
218.7 ± 0.3	Combustion of titanium in oxygen at 610°	1945	Lipkes	/120/
225.5 (273°K)	—	1951	Humphrey	/88/

Bichowsky, Rossini /120a/, and Kubaschewski /89/ give ΔH^0_{298} = −219.0± 1.5 kcal/mole for TiO_2 rutile; Brewer /74/ gives ΔH^0_{298} = −225.6 kcal/mole for the same compound.

Entropy of formation of TiO_2. According to Brewer /74/, the entropy of formation of TiO_2 is given by ΔS^0_{298} = −44.2 cal/mole · degree. The entropy given by Kubaschewski and Hopkins /79/ for the oxidation of titanium to titanium dioxide by oxygen at 76 to 100 mm Hg and 400 to 600°

is given by $\Delta S^0_{298} = -22.8$ cal/mole·degree. Kubaschewski and Hopkins note however that this value is not accurate. According to Kelley /113/, the entropy of formation of TiO_2 is given by $\Delta S^0_{298} = -43.7$ cal/mole·degree.

Free energy of formation of TiO_2. According to the data of Humphrey /88/, the free energy of formation of TiO_2 is given by $\Delta F = -212.3$ kcal/mole at 0°. Brewer /74/ gives $\Delta F^0_{298} = -212.4$ kcal/mole. Kubaschewski /89/ derived the following equation:

$$\Delta F^0_T = -219{,}400 - 3.46\,T \log T + 54.15\,T,$$

where T is the temperature in degrees absolute. It is valid from 298 to 2000°K, and its accuracy is within 6 kcal. For the free energy of formation of TiO_2, Kelley /113/ gives $\Delta F^0_{298} = -205{,}670$ cal/mole.

16. SULFIDES OF TITANIUM

The following sulfides of titanium are known to exist: Ti_3S_5, Ti_2S_3, Ti_3S_4, Ti_4S_5, TiS_3, and TiS_2 /121—123/. Biltz et al. /122/ report the non-stoichiometric sulfides: $TiS_{1.50}$, $TiS_{1.5}$, and $TiS_{1.28}$. This reference book however contains thermodynamic data on only two titanium sulfides: TiS_2 and TiS_3.

Titanium disulfide TiS_2 ($M = 112.132$)

Crystal structure of TiS_2. According to Jeannin and Benard /124/, TiS_2 has a hexagonal crystal structure. Laves /125/ reports that solid TiS_2 has a CdI_2 type crystal structure, whose unit cell has the following parameters: $a = 3.40$ Å and $c = 5.69$ Å.

Density and molar volume of TiS_2. Biltz et al. /122/ gave the density as 3.22 g/cm^3 at 20°. Luchinskii /17/ gives the same value at 25°.

The molar volume of TiS_2 is 32.5 cm^3/mole (Oftedal /126/) and 34.8 cm^3/mole (Biltz et al. /122/).

Transition temperature of TiS_2. According to Todd and Coughlin /127/, the transformation of α- to β-TiS_2 occurs at 420°K.

Heat capacity of TiS_2. The heat capacity of titanium disulfide, TiS_2, at lower temperatures was determined by Todd and Coughlin /127/. Their data are presented in Table 132.

TABLE 132

Heat capacity of TiS_2 at lower temperatures /127/

T, °K	C_p cal/deg·mole	T, °K	C_p cal/deg·mole	T, °K	C_p cal/deg·mole
53.91	3.242	114.88	9.347	216.23	14.61
57.79	3.630	124.56	10.13	226.30	14.83
62.01	4.067	136.11	10.97	236.24	15.07
66.11	4.493	146.24	11.60	245.81	15.26
70.64	4.968	156.04	12.18	256.28	15.48
75.53	5.522	166.00	12.72	266.28	15.68
79.83	5.973	176.01	13.19	276.43	15.84
83.94	6.402	186.03	13.62	288.07	16.06
94.97	7.516	196.17	13.97	296.66	16.23
104.46	8.470	206.21	14.32	298.16	(16.23)

Heat content of TiS_2. Data on the molar heat content of titanium disulfide above 298°K, according to Todd and Coughlin /127/, are presented in Table 133.

TABLE 133

Heat content of TiS_2, kcal/mole · deg /127/

T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$
350	0.860	500	3.540	900	11.000
400	1.180	600	5.350	1000	12.970
420	2.180 (α)	700	7.210	1100	15.020
420	2.180 (β)	800	9.090		

The data of Todd and Coughlin /127/ conform to the following equations: for TiS_2 (α) (accuracy 1%, 298 to 420°K)

$$H_T - H^0_{298} = 8.08T + 13.67 \cdot 10^{-3}T^2 - 3624,$$

and for TiS_2 (β) (accuracy 0.3%, 420 to 1100°K)

$$H_T - H^0_{298} = 14.99T + 2.57 \cdot 10^{-3}T^2 - 4569.$$

Entropy of TiS_2. From the heat capacity data of Todd /128/ for solid TiS_2, Kelley /113/ calculated its entropy from 53* to 298°K. He then obtained S^0_{298} = 18.73 cal/mole · degree by adding S^0_{51} = 1.38 (extrapolated result) and $S^0_{298} - S^0_{51}$ = 17.35 cal/mole · degree (experimental).

Todd and Coughlin /127/ determined the entropy of TiS_2 from 298 to 1100°K. Their results are presented in Table 134.

TABLE 134

Entropy of TiS_2, cal/mole · deg /127/

T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$	T, °K	$S_T - S^\circ_{298}$
350	2.65	500	9.05	900	19.98
400	5.16	600	12.35	1000	22.05
420	6.09 (α)	700	15.22	1100	24.00
420	6.09 (β)	800	17.73		

Heat of formation of TiS_2. Kubaschewski and Evans /65/ give the heat of formation of TiS_2 as 80.0 ± 20.0 kcal/mole.

Titanium trisulfide TiS_3 (M = 144.098)

Crystal structure of TiS_3. Crystallographic analyses of TiS_3 carried out by Jeannin and Benard /124/ showed that this compound has a monoclinic structure with the following unit cell parameters: a = 4.97 ± 0.01 Å, b = 3.42 ± 0.01 Å, and β = 97°10'. There are two molecules of TiS_3 to each unit cell.

Density and molar volume of TiS_3. According to Biltz et al. /122/, the density of TiS_3 is 3.22 g/cm^3.

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* [Probably 51 is intended.]

The molar volume of TiS_3 is given by Oftedal /126/ as 33.8 cm^3/mole, and by Biltz et al. /122/ as 44.8 cm^3/mole.

Dissociation pressure of TiS_3. The dissociation pressure of TiS_3 was determined by Biltz /122/. His data are presented in Table 135. $\overline{\Sigma P}$ is the total pressure of sulfur vapor, and P_{S_2}, P_{S_6}, and P_{S_8} are the partial pressures of S_2, S_6, and S_8.

TABLE 135

Total and partial pressures of sulfur vapor in mm Hg /122/

t, °C	$\overline{\Sigma P}$	P_{S_2}	P_{S_6}	P_{S_8}
500	91	3.85	43	9.5
525	228	83	112.5	27.5
528	349	122	181	46
551	529	173	280	76

Heat of dissociation of TiS_3. Biltz and co-workers /122/ determined the heat of dissociation of TiS_3 at 525°.

for $2TiS_3\,(s) = 2TiS_2\,(s) + S_2\,(g)$ $\Delta H = -38$ cal;

for $6TiS_3\,(s) = 6TiS_2\,(s) + S_6\,(g)$ $\Delta H = -47$ cal;

for $8TiS_3\,(s) = 8TiS_2\,(s) + S_8\,(g)$ $\Delta H = -52$ cal.

Heat of formation of TiS_3. The heat of formation of TiS_3 from TiS_2 and rhombic sulfur, according to the equation ($TiS_2(s) + S_{rhombic} = TiS_3(s)$) was determined by Biltz /122/ who found $\Delta H = +4$ kcal.

17. HALIDES OF TITANIUM

Fluorides of titanium

There are three titanium fluorides: TiF_2, TiF_3, and TiF_4. Only thermodynamic data for the last two compounds are given below. Unfortunately, almost no data for TiF_2 are available. Rossini and co-workers /32/ give $\Delta H^\circ_{298} = -198$ kcal/mole for the heat of formation of TiF_2.

Titanium trifluoride TiF_3 ($M = 104.9$)

Crystal structure of TiF_3. The crystals of this compound have a rhombohedral structure with the parameters $a = 5.52$ Å and $\alpha = 58.88°$, and contain two molecules per cell /129/.

Density of TiF_3. The density of TiF_3 was determined by Ehrlich and Pietzka /129/ by means of pycnometric and X-ray methods which gave 2.98 and 3.00 g/cm^3, respectively.

Heat of formation of TiF_3. Rossini and co-workers /32/ give $\Delta H^\circ_{298} = -315$ kcal/mole for the heat of formation of TiF_3.

Titanium tetrafluoride TiF_4 (M = 123.9)

Density and molar volume of TiF_4. According to Ruff and Plato /130/, the density of TiF_4 is 2.833 and 2.798 g/cm^3 at 11° and 20.5°, respectively. Luchinskii /17/ gives 2.8362 and 2.7995 g/cm^3 at 10° and 20°, respectively.

According to Ruff and Plato /130/, the molar volume of TiF_4 is 45.8 cm^3/mole.

Vapor pressure of TiF_4. The following equation for the vapor pressure of solid TiF_4 was derived from the measurements of Hall and co-workers /131/.

$$\log P(\text{atm}) = -\frac{5331.51}{T} - 2.567 \log T + 16.631.$$

Boiling point of TiF_4. According to Ruff and Plato /130/, the boiling point of TiF_4 is 284°. The same value is given by Rossini and co-workers /32/. Hall et al. /131/ give 556.3°K at one atmosphere pressure.

Heat of vaporization of TiF_4. Hall and co-workers /131/ investigated the heat of vaporization of TiF_4 and obtained 22.87±0.28 kcal/mole and 21.55 ± 0.28 kcal/mole at 298 and 556.3°K, respectively.

Entropy of vaporization of TiF_4. The entropy of vaporization was calculated by Hall and co-workers /131/, who gave $\Delta S^0_{vap_{298}} = 41.92 \pm 0.40$ e.u. and $\Delta S^0_{vap_{556.3}} = 38.74 \pm 0.40$ e.u., at 298 and 556.3°K, respectively.

Entropy of TiF_4. The absolute entropies of solid and gaseous TiF_4 were determined by Hall et al. /131/ and are given by $S^0_{298} = 31.3 \pm 0.40$ e.u. and $S^0_{298} = 73.2$ e.u., respectively.

Heat of formation of TiF_4. Rossini et al. /32/ give $\Delta H^0_{298} = -370$ kcal/mole for the heat of formation of solid TiF_4.

CHLORIDES OF TITANIUM

The following chlorides of titanium are known: TiCl, $TiCl_2$, $TiCl_3$, and $TiCl_4$. The heat of formation of gaseous TiCl is given as $\Delta H^0_{298} = +122$ kcal/mole /32/.

Titanium dichloride $TiCl_2$ (M = 118.814)

Crystal structure of $TiCl_2$. Solid $TiCl_2$ has a crystal structure of the CdI_2 type with the following unit cell parameters: a = 3.56 Å and b = 5.88 Å /6/.

Boiling point of $TiCl_2$. Kubaschewski and Evans /65/ give the boiling point of titanium dichloride as 1000°.

Sublimation and disproportionation pressures of $TiCl_2$. Funaki and Uchumura /132/ derived the following equation for the sublimation pressure of $TiCl_2$:

$$\log P(\text{mm Hg}) = -\frac{8500}{T} + 9.30.$$

The disproportionation of $TiCl_2$, according to equations

$$3TiCl_2 = Ti + 2TiCl_3 \text{ and } 2TiCl_2 = Ti + TiCl_4,$$

was studied above 950°K by Skinner and Ruehrwein /133/. The partial pressures of $TiCl_3$, $TiCl_2$, and $TiCl_4$, and the sum of these pressures are presented in Table 136.

TABLE 136

Calculated disproportionation pressure of $TiCl_2$ in mm Hg /133/

Temperature, °K	Total pressure, P_{exptl}	P_{TiCl_3}	P_{TiCl_2}	P_{TiCl_4}	Total pressure, P
977	16.3	6	8	1	15
1009	36.3	11	18	1	30
1041	66.7	23	36	3	62
1071	126.2	41	66	5	112

Heat capacity of $TiCl_2$. Clifton and Macwood /134/ derived equations for the molar heat capacities of titanium chlorides. The equation for solid $TiCl_2$ is:

$$C_p = 17.0 + 2.76 \cdot 10^{-3} T - 0.70 \cdot 10^5 T^{-2}.$$

Heat, entropy, and free energy of sublimation and disproportionation of $TiCl_2$. The sublimation and disproportionation of solid $TiCl_2$ from 800 to 900° were studied by Farber and Darnell /135/ by means of the effusion method. At a mean temperature of 850°, the following values were obtained for the process $TiCl_2(s) \rightarrow TiCl_2(g)$: $L_{subl} = 46.8$ kcal/mole and $\Delta S_{subl} = 30.7$ cal/mole · degree. For the disproportionation process according to reaction

$$2TiCl_2(s) = TiCl_4(g) + Ti(s)$$

at 850°, the same authors found $L_{disp} = 49.5$ kcal/mole and $\Delta S_{disp} = 32.2$ cal/mole · degree. Disproportionation of $TiCl_2$ at this temperature may also proceed according to the equation $3TiCl_2(s) = 2TiCl_3(g) + Ti(s)$. In this case, the heat and entropy of disporportionation of $TiCl_2$ are given by $L_{disp} = 87.2$ kcal/mole and $\Delta S_{disp} = 30.7$ cal/mole · degree, respectively.

According to Funaki and Uchumura /132/, the free energy of disproportionation of $TiCl_2$ is

$$\Delta F_T^\circ = 39.0 \cdot 10^3 - 29.5\, T \text{ cal}.$$

Heat content of $TiCl_2$. The heat content of solid and gaseous $TiCl_2$, according to Skinner and Ruehrwein /133/, is presented in Table 137.

TABLE 137

Heat content of solid and gaseous $TiCl_2$, in cal/mole /133/

T, °K	$H_T - H_0^\circ$	
	$TiCl_2$ (s)	$TiCl_2$ (g)
298	3800	3000
500	7500	5600
1000	17000	12700
1500	—	20400

TABLE 138

The Φ^* function for $TiCl_2$ in cal/mole · deg /8/

T, °K	Φ^*	
	$TiCl_2$ (s)	$TiCl_2$ (g)
298	12.7	58.5
500	19.7	64.1
1000	30.7	72.4
1500	—	77.6
2000	—	81.3

Entropy of $TiCl_2$. The entropy of $TiCl_2$ is given by S^0_{298} = 24.7 cal/mole · degree and S^0_{298} = 65.9 e.u. for solid and gaseous titanium dichloride, respectively. These results were obtained by Altman and coworkers /137/. According to Hartmann and Rinck /138/, the entropy of solid $TiCl_2$ is given by S^0_{298} = 26.2 ± 2.1 cal/degree · mole. For the entropy of solid $TiCl_2$, Kubaschewski and Evans /65/ give S^0_{298} = 29.0 ± 4.0 cal/mole · degree.

Free energy function of $TiCl_2$. The Φ' function $-\frac{F^0_T - H^0_0}{T}$ for solid and gaseous titanium dichloride is given in Table 138 /133/.

Heat of formation of $TiCl_2$. The heat of formation of solid and gaseous $TiCl_2$ is given in Table 139.

TABLE 139

Heat of formation of gaseous and solid titanium dichloride

$-\Delta H^0_{298}$, kcal/mole	Year	Author	Reference
		Solid $TiCl_2$	
123.3 ± 0.7 123.7 ± 1.0	1956	Clifton, Macwood	/134/
118.7*	1955	Skinner, Ruehrwein	/133/
118.3	1955	Skinner, Ruehrwein	/133/
120.1	1956	Krive et al.	/136/
120.6	1956	Altman et al.	/137/
121.0 ± 1.1	1957	Hartmann, Rinck	/138/
		Gaseous $TiCl_2$	
69.1* 69.5	1955	Skinner, Ruehrwein	/133/
69.4	1956	Altman et al.	/137/

* At 0°.

For the heat of formation of solid $TiCl_2$, Rossini et al. /32/ give ΔH°_{298} = −114 kcal/mole.

Titanium trichloride $TiCl_3$ (M = 154.271)

Crystal structure of $TiCl_3$. Titanium trichloride has an AsI_3 type crystal lattice with the following parameters: a = 6.82 Å and α = 53°20 /65/.

Sublimation and disproportionation pressure of $TiCl_3$. Clifton and Macwood /134/, using the effusion method, derived the following empirical relationships to describe the vapor pressure of reaction

$$2TiCl_3\,(s) = TiCl_2\,(s) + TiCl_4\,(g),$$

from 628 to 823°K

$$\log P(\text{mm Hg}) = -\frac{8296}{T} + 10.401,$$

and from 593 to 821°K

$$\log P(\text{mm Hg}) = -\frac{6987}{T} + 8.407.$$

Skinner and Ruehrwein /133/ studied the disproportionation of $TiCl_3$ at high temperatures according to the reaction $2TiCl_3 = TiCl_4 + TiCl_2$. The total and partial pressures of the reactants and products of this reaction are shown in Table 140.

TABLE 140

Total and partial pressures of the disproportionation reaction of $TiCl_3$ in mm Hg /133/

T, °K	Total pressure P	P_{TiCl_3}	P_{TiCl_2}	P_{TiCl_4}
802	16.1	4.0	0.0	12.1
849	54.1	15.2	0.2	38.7
863	75.5	21.9	0.4	53.2
900	182.0	58.0	1.0	123.0
928	339.0	105.0	2.0	232.0

The disproportionation reaction between 600 and 740°K, $2TiCl_3 = TiCl_4 + TiCl_2$, was also studied by Farber and Darnell /139/. The partial pressure of $TiCl_4$ fluctuated between 0.005 at 636°K and 0.200 mm Hg at 732°K, and the partial pressure of $TiCl_3$ varied from 0.0002 to 0.0100 mm Hg in the same temperature range.

Funaki and Uchumura /132/ studied the reaction $TiCl_2(s) + TiCl_4(g) = 2TiCl_3(s)$ below 450° and found that the disproportionation pressure of $TiCl_3(s)$ obeys the following equation:

$$\log P(\text{mm Hg}) = -\frac{7000}{T} + 10.5.$$

Heat capacity of $TiCl_3$. According to Clifton and Macwood /134/, the molar heat capacity of $TiCl_3$ may be expressed by the following two equations:

for solid $TiCl_3$ $\quad C_p = 23.0 + 4.0 \cdot 10^{-3}T - 1.7 \cdot 10^5 T^{-2}$,

and for gaseous $TiCl_3$

$$C_p = 19.1 + 0.18 \cdot 10^{-3}T - 1.7 \cdot 10^5 T^{-2},$$

where T is the temperature in degrees absolute.

Heat capacity change during sublimation of $TiCl_3$. According to Clifton and Macwood /134/, the heat capacity change during sublimation of $TiCl_3$ (from 298 to 688°K) is governed by the following equation:

$$\Delta C_p = -3.9 - 3.8 \cdot 10^{-3}T.$$

Farber and Darnell /139/ calculated an approximate value of −9 cal/mole · degree for ΔC_P during sublimation of $TiCl_3$.

Heat of sublimation of $TiCl_3$. From sublimation pressure data, Clifton and Macwood /134/ calculated the heat of sublimation of $TiCl_3$ as 42.0 ± 0.5 kcal/mole. The same authors /134/ derived the following equation for the heat of sublimation of $TiCl_3$ from 298 to 688°K.

$$L_{subl} = 43{,}300 - 3.9T - 1.9 \cdot 10^{-3}T^2.$$

Farber and Darnell /139/ found experimentally that the heat of sublimation of $TiCl_3$ is 42 kcal/mole at 298°K and 39 kcal/mole at 688°K.

Entropy of sublimation of $TiCl_3$. According to Clifton and Macwood /134/, the entropy of sublimation of $TiCl_3$ is given by ΔS^0_{subl} = 41.6 cal/mole · degree at 298°K. Farber and Darnell /139/ quote 37.e.u. and 31 e.u. at 298 and 688°K, respectively.

Free energy of sublimation of $TiCl_3$. For the free energy of sublimation of $TiCl_3$ at 298°K, Clifton and Macwood /134/ give ΔF^0_{298} = 29.6 ± 1.0 kcal/mole. The variation of the free energy with temperature /134/ is given by the following equation:

$$\Delta F^\circ_{subl} = 43{,}300 + 3.9\,T \ln T + 1.9 \cdot 10^{-3} T^2 - 68.71\,T,$$

valid from 298 to 688°K.

According to Farber and Darnell /139/, the free energy of sublimation of $TiCl_3$ is given by ΔF^0_{subl} = 17.6 kcal/mole. The same workers /139/ derived the following equation for the free energy of sublimation of $TiCl_3$ from 298 to 688°K:

$$\Delta F^\circ_{subl} = 43{,}000 - 9\,(T - 298) - \left(37 - 9 \ln \frac{T}{298}\right).$$

Heat capacity difference for disproportionation of $TiCl_3$. For the disproportionation reaction of $TiCl_3$, according to the reaction $2TiCl_3(s) = TiCl_2(s) + TiCl_4(g)$, Clifton and Macwood /134/ derived the following equation for the heat capacity difference:

$$\Delta C_p = -3.55 - 5.00 \cdot 10^{-3} T + 0.34 \cdot 10^5 \cdot T^{-2},$$

valid from 593 to 821°K.

According to Farber and Darnell /139/, ΔC_P = 8.1 cal/mole · degree.

Heat of disproportionation of $TiCl_3$. Hartmann and Rinck /138/ used the cooling method to study the equilibrium disproportionation of $TiCl_3$ from 540 to 700°, according to the reaction $2TiCl_3 = TiCl_2 + TiCl_4$. It was found that the partial pressure of $TiCl_4$ increases very considerably with increasing temperature. It is concluded therefore that this disproportionation is endothermic. The average heat of disproportionation over the investigated temperature range is given by ΔH^0 = 35.5 ± 0.5 kcal/mole.

Farber and Darnell /139/ studied the disproportionation of $TiCl_3$ from 600 to 740°, according to the reaction $2TiCl_3 = TiCl_4 + TiCl_2$, and found the heat of disproportionation L_{disp} to be 38 and 35 kcal/mole at 298°K and 675°K, respectively.

Clifton and Macwood /134/ studied the disproportionation reaction $2TiCl_3 = TiCl_2(s) + TiCl_4$ from 593 to 821°K, and derived the following equation:

$$L_{disp} = 40{,}000 - 3.55T - 2.5 \cdot 10^{-3} T^2 - 0.34 \cdot 10^5 T^{-2}.$$

Entropy of disproportionation of $TiCl_3$. Hartmann and Rinck /138/ determined the entropy of disproportionation for the reaction $2TiCl_3 = TiCl_2 + TiCl_4$ and obtained as an average value ΔS^0 = 36.2±0.6 cal/degree · mole from 540 to 700°. According to Farber and Darnell /139/, the entropy of disproportionation is 38 e.u. and 32 e.u. at 298 and 675°K, respectively.

Free energy of disproportionation of $TiCl_3$. Funaki and Uchumura /132/ determined the free energy of disproportionation of $TiCl_3$

according to the reaction $2TiCl_3 = TiCl_2 + TiCl_4$ and obtained $\Delta F^\circ_{disp} = 31,990 - 33.22\,T$ cal/2 moles of $TiCl_3$. Farber and Darnell /139/ derived the following equation, valid from 600 to 740°K:

$$\Delta F^\circ_{disp} = 38,000 - 8.1\,(T - 298) - T\left(38 - 8.1\,\ln\frac{T}{298}\right).$$

From the equation the authors found $\Delta F^\circ_{disp} = 13.5$ kcal/mole at 675°.

The data of Clifton and Macwood /134/ on the free energy of disproportionation of $TiCl_3$, according to the reaction $2TiCl_3\,(s) = TiCl_2\,(s) + TiCl_4\,(g)$ at 593 to 821°K, can be expressed by the following equation:

$$\Delta F^\circ_{disp} = 40,000 + 3\,55\,T\ln T + 2.5\cdot 10^{-3}T^2 - 0.17\cdot 10^5 T^{-1} - 67.75\,T.$$

Heat content of $TiCl_3$. The heat content of solid and gaseous titanium $TiCl_3$ is given in Table 141 /133/.

TABLE 141

Heat content of $TiCl_3$ /133/

T, °K	$H_T - H^\circ_0$, cal/mole	
	$TiCl_3$ (s)	$TiCl_3$ (g)
298	4500	4200
500	9200	8000
1000	21800	17700
1500	—	27600

TABLE 142

Φ^* function for $TiCl_3$ /133/

T, °K	Φ^*, cal/mole·deg.	
	$TiCl_3$(s)	$TiCl_3$ (g)
298	19.4	63.7
500	28.2	71.4
1000	42.2	82.9
1500	—	90.1

TABLE 143

Heat of formation of $TiCl_3$

Heat of formation, $-\Delta H^0_{298}$, kcal/mole	Year	Author	Reference
Solid $TiCl_3$			
161.1	1954	Schafer et al.	/140/
161.6			
172.2 ± 0.7	1956	Clifton, Macwood	/134/
170.0 ± 0.8	1955	Skinner, Ruehrwein	/133/
170.1*			
169.1	1956	Krive et al.	/136/
170.7	1956	Altman et al.	/137/
Liquid $TiCl_3$			
191.0 ± 3.0	1956	Clifton, Macwood	/134/
Gaseous $TiCl_3$			
127.7*	1955	Skinner, Ruehrwein	/133/
128.0			
130.2 ± 1.4	1956	Clifton, Macwood	/134/
128.7	1956	Altman et al.	/137/

* At 0°K.

Entropy of $TiCl_3$. According to Altman et al. /137/, the entropies of solid and gaseous $TiCl_3$ are given by S^0_{298} = 34.4 cal/mole · degree and S^0_{298} = 74.9 cal/mole · degree, respectively. For solid $TiCl_3$, Kubaschewski and Evans /65/ give S^0_{298} = 39.0 ± 4.0 cal/mole · degree.

Free energy function of $TiCl_3$. Skinner and Ruehrwein /133/ give the following values for the Φ' function of solid and gaseous $TiCl_3$ from 298 to 1500°K (Table 142).

Heat of formation of $TiCl_3$. The heat of formation of solid, liquid, and gaseous $TiCl_3$ is given in Table 143.

Titanium tetrachloride $TiCl_4$ (M = 189.728)

Crystal structure of $TiCl_4$. The $TiCl_4$ molecule forms a regular tetrahedron with the titanium atom in the center and the chlorine atoms at the apices. The distance between the individual chlorine atoms is 3.61 Å. There is one molecule of $TiCl_4$ per cell.

Density and molar volume of $TiCl_4$. According to Stiefelhagen /141/, the density of $TiCl_4$ at 18° is 1.761 g/cm^3. The densities of $TiCl_4$ from −10 to 100° are given below /17/.

Temperature, °C	-10	0	+10	20	40	100
Density, g/cm^3	1.7784	1.7609	1.7446	1.7277	1.6937	1.5891

The density of $TiCl_4$ can be expressed by the following equations:

$$d_t = 1.767 - 0.00162t \text{ /142/}$$

$$d_t = 1.7606 - 0.00169t - 7.3 \cdot 10^{-7}t^2 - 2.0 \cdot 10^{-9}t^3 \text{ /17/.}$$

According to Hildebrand and Carter /143/, the molar volume of $TiCl_4$ is 110.5 cm^3/mole.

Melting point of $TiCl_4$. The melting point of $TiCl_4$, according to different authors, is given in Table 144.

TABLE 144

Melting point of $TiCl_4$

Melting point, °C	Year	Author	Reference
-23	1904	Emich	/144/
-30	1922	Latimer	/145/
-23	1923	Biltz, Meinecke	/146/

Kelley /147/, Luchinskii /17/, Kubaschewski and Evans /65/, and Rossini et al. /32/ give the melting point of $TiCl_4$ as −23°.

Boiling point of $TiCl_4$. The boiling point of $TiCl_4$ as determined by different authors is given in Table 145.

Luchinskii /17/ gives the normal boiling point of $TiCl_4$ as 135.8°. The same temperature is given by Rossini and co-workers /32/. Kubaschewski and Evans /65/ consider 136° to be the best value.

TABLE 145

Boiling point of $TiCl_4$

Boiling point, °C	P, mm Hg	Year	Author	Reference
136	—	1904	Stähler	/148/
134.8	735	1904	Emich	/144/
136	—	1907	Ellis	/149/
136	—	1907	Vigouroux, Arrivant	/150/
136.5	—	1910	Hunter	/151/
136.5	761	1923	Biltz, Meinecke	/146/
136	750	1923	Bond, Beach	/152/
136	753	1929	Garner, Sudgen	/142/
136.5	760	1954	Schäfer, Zeppernik	/153/
135.5	739.6			

Vapor pressure of $TiCl_4$. The vapor pressure of liquid titanium tetrachloride was measured by Arii /154, 155/. His data are presented in Tables 146 and 147.

TABLE 146

Vapor pressure of liquid $TiCl_4$ in mm Hg /154, 155/

t, °C	P	t, °C	P	t, °C	P
20	10.5	60	62.15	100	264.5
30	16.7	70	92.95	110	367.75
40	26.5	80	134	120	493.5
50	41.15	90	190	135	740.75

TABLE 147

Vapor pressure of $TiCl_4$ /154, 155/

T, °C	Vapor pressure, atm	T, °C	Vapor pressure, atm	T, °C	Vapor pressure, atm
<255.5(s)	0.001	337	0.1	383.5	0.5
255.5(l)	0.001	361.5	0.25	409	1.0
290	0.01				

According to Arii, the vapor pressure of $TiCl_4$ from 20 to 135° /154, 155/, is given by the equation:

$$\log P(\text{mm Hg}) = 7.64433 - \frac{1947.6}{T}$$

For the vapor pressure of $TiCl_4$ from 293 to 408°K, Kelley /56/ derived the following equation:

$$\log P(\text{mm Hg}) = -\frac{2850}{T} - 5.90 \log T + 25.00.$$

Schäfer and Zeppernik /153/, using an isoteniscope (a static method), measured the vapor pressure of $TiCl_4$ from 40 to 48°. Their vapor pressure data (±0.0007, 40 to 48°) fit the following equation:

$$\log P(\text{mm Hg}) = 8.0015 - \frac{2.0775 \cdot 10^3}{T}.$$

The vapor pressure measurements of Schafer and Zeppernik /153/ are more accurate than those of Arii.

Stull /157/ gives the following values for the vapor pressure of $TiCl_4$:

Temperature, °C	-13.9	+9.4	21.3	34.2	48.4	58.0	71.0	90.5	112.7	136.0
Vapor pressure, mm Hg	1	5	10	20	40	60	100	200	400	760

We consider the values of Stull /157/ to be the most reliable.

Heat capacity of $TiCl_4$. The molar heat capacity of $TiCl_4$, according to the data of Latimer /145/, is given in Table 148.

TABLE 148

Molar heat capacity of $TiCl_4$ cal/mole · deg /145/

T, °K	C_p	T, °K	C_p	T, °K	C_p
86.7	4.26	194.6	6.19	251.6 (l)	7.26*
92.8	4.40	231.8	6.31	294.3	7.32*
99.3	4.54	247.7 (s)	6.21		

* These values are for liquid $TiCl_4$, the others for solid $TiCl_4$.

Molar heat capacities of solid and liquid $TiCl_4$ at lower temperatures, according to Kelley /71/, are quoted below:

Temperature, °K	100	150	200	298.16
Heat capacity cal/mole · deg	22.77*	27.14*	30.12*	37.53**

Table 149 shows the heat capacities of liquid and gaseous $TiCl_4$ above room temperature.

TABLE 149

Molar heat capacity of $TiCl_4$

Heat capacity C_p cal/mole · deg	Accuracy of determination, ± %	Temperature range, °K	Author	Reference
		Liquid		
$C_p = 36.0$	—	293 — 408	Arii	/155/
$C_p = 35.7$	3	285 — bp	Kubaschewski, Evans	/ 65/
		Gaseous		
$C_p = 24.5$	—	293 — 408	Arii	/155/
$C_p = 25.45 + 0.24 \cdot 10^{-3}T - 2.36 \times 10^5 T^{-2}$	—	298 — 2000	Herman	/158/
$C_p = 24.61 + 1.54 \cdot 10^{-3}T - 1.94 \times 10^5 T^{-2}$	1.5	298 — 575	Herman; Spencer	/158/; /159/

* For solid $TiCl_4$.

** For liquid $TiCl_4$.

For the heat capacity of liquid and gaseous $TiCl_4$ at 298°K, Rossini and co-workers /32/ give $C_P = 22.88$ and $C_P = 37.5$ cal/mole·degree, respectively.

Heat of fusion of $TiCl_4$. The specific heat of fusion of $TiCl_4$, according to different authors, is presented in Table 150.

TABLE 150

Specific heat of fusion of $TiCl_4$ at 25°

Specific heat of fusion cal/g	Year	Author	Reference
1.177	1918	Narbut	/160/
1.177	1922	Latimer	/145/
1.290	1934	Nasu	/162/

Biltz and Meinecke /146/ studied the system $TiCl_4 - Cl_2$ and obtained a heat of fusion of $TiCl_4$ of 2120 cal/mole.

Nasu /161, 162/ studied the systems $TiCl_4 - CCl_4$, $TiCl_4 - SbCl_4$, $TiCl_4 - SiCl_4$, and $TiCl_4 - SnCl_4$. Calculations based on studies of the first three systems led to heat of fusion values of 2340, 2170, and 2420 cal/mole, respectively, while the fourth system led to a much higher value, i.e., 3110 cal/mole. The average of these four values is 2260 cal/mole, which is only slightly different from the value of 2230 cal/mole, obtained by Latimer /145/. Kelley considers the average of the last two quoted values, i.e., 2240 cal/mole, to be the true heat of fusion of $TiCl_4$.

The system $TiCl_4 - SO_2$ was investigated by Bond and Stephans /163/. These authors obtained for the heat of fusion of $TiCl_4$ the higher value 2720 cal/mole.

Kubaschewski and Evans /65/ consider Latimer's value /145/ ($L_{fus} = 2.3 \pm 0.1$ kcal/mole) to be the most reliable. Rossini and co-workers /32/ give the value adopted by Kelley, i.e., 2.24 kcal/mole.

Entropy of fusion of $TiCl_4$. Rossini and co-workers /32/ give $\Delta S_{fus} = 9.0$ cal/mole·degree at 250°K.

Heat capacity change during vaporization of $TiCl_4$. The heat capacity change during vaporization of $TiCl_4$ from 293 to 408°K is given by $\Delta C_P = -11.5$ cal/mole·degree /156/.

Heat of vaporization of $TiCl_4$. According to Arii /154/, the heat of vaporization of $TiCl_4$ is 8960 cal/mole at 25° and 8620 cal/mole at 136°.

Kelley /156/, referring to the results of Arii /154, 155/, gives 9622 and 8346 cal/mole at 298 and 409°K, respectively. Kubaschewski and Evans /65/ consider the values adopted by Kelley /156/, i.e., $L_{vap} = 9.6 \pm 0.2$ kcal/mole at 25° and $L_{vap} = 8.4 \pm 0.2$ kcal/mole at the boiling point of $TiCl_4$, to be the most reliable.

According to Schäfer and Zeppernik /153/, the heat of vaporization of $TiCl_4$ is 8.65 kcal/mole at 136.5°. Rossini et al. /32/ give 8.4 kcal/mole at 135.8°.

The heat of vaporization of $TiCl_4$ from 293 to 408°K obeys the following equation /156/:

$$L_{vap} = 13{,}050 - 11.5T \text{ cal/mole.}$$

Entropy of vaporization of $TiCl_4$. According to Schäfer and Zeppernik /153/, the entropy of vaporization, ΔS°_{vap}, of $TiCl_4$ is 21.12 cal/mole · degree at 136.5°.

The values given by Kelley /156/ and Rossini and co-workers /32/ are 24.0 cal/mole · degree and 20.5 cal/mole · degree, respectively. Both values refer to a temperature of 409°K.

Free energy of vaporization of $TiCl_4$. The standard free energy of vaporization of $TiCl_4$ is given by $\Delta F^\circ_{298} = 2459$ cal/mole /156/.

The variation of free energy of vaporization of $TiCl_4$ with temperature (293 to 408°K) obeys the following equation /156/:

$$\Delta F^\circ_{vap} = 13{,}050 + 26.5\,T \log T - 101.1\,T.$$

Heat content of $TiCl_4$. Kelley /62/ considers the results of Herman /158/ on the heat content of liquid and gaseous $TiCl_4$ to be the most reliable. They are presented in Table 151.

TABLE 151

Heat content of $TiCl_4$, cal/mole /158, 62/

T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$	T, °K	$H_T - H^\circ_{298}$
400	2395	800	12340	1400	27665
500	4830	900	14880	1600	32800
600	7310	1000	17425	1800	39945
700	9815	1200	22535	2000	43090

The data of Herman /158/ fit the following equation (accuracy of 0.5%, 298 to 2000°K):

$$H^\circ_T - H^\circ_{298} = 25.45\,T + 0.12 \cdot 10^{-3} T^2 + 2.36 \cdot 10^5 T^{-1} - 8390.$$

Skinner and Ruehrwein /133/ later obtained the heat content of solid and gaseous $TiCl_4$ values quoted in Table 152.

TABLE 152

Heat content of $TiCl_4$ /133/

T, °K	$H_T - H^0_0$, cal/mole	
	$TiCl_4$ (l)	$TiCl_4$ (g)
298	9100	5100
500	—	10,000
1000	—	22,800
1500	—	35,600

Entropy of $TiCl_4$. The standard entropies of liquid and gaseous $TiCl_4$ are presented in Table 153.

Farber and Darnell /168/ studied the equilibrium of the reaction TiO_2 (s) + 4HCl (g) = $TiCl_4$ + $2H_2O$ at 1100°K. They found that for gaseous

$TiCl_4$ at this temperature S° = 124 cal/mole · degree. The same authors /168/ calculated the entropy of gaseous $TiCl_4$ from spectroscopic data and obtained S° = 117 cal/mole · degree at 1100°K.

For the entropy of liquid $TiCl_4$, Kubaschewski and Evans /65/ and Rossini and co-workers /32/ give S°_{298} = 60.0 ± 0.6 cal/mole·degree and S°_{298} = 60.4 cal/mole · degree, respectively.

Kubaschewski and Evans /65/ give S°_{298} = 84.4 ± 0.1 cal/mole · degree for the entropy of gaseous $TiCl_4$. Rossini and co-workers /32/ also consider this to be the most reliable value.

TABLE 153

Entropies of liquid and gaseous $TiCl_4$

Entropy S^0_{298}, cal/mole · deg	Method	Year	Author	Reference
	Liquid $TiCl_4$			
59.51	Calculated from heat capacity data of $TiCl_4$	1922	Latimer	/145/
60.3 ± 1.5	Calculated from vapor pressure and entropy data for gaseous $TiCl_4$	1933 1950	Jost, Blair Kelley	/164/ / 71/
	Gaseous $TiCl_4$			
84.3 ± 1.0	Calculated from spectroscopic data	1936 1931	Brockway Paramasivan	/165/ /166/
84.4	As above			
81.5	Calculated from Nernst's law	1933	Jost, Blair	/164/
82.1 ± 0.5	Calculated from standard entropies of the reactants and products in the equations: $TiCl_4 + 2H_2 + \frac{1}{2}N_2 = TiN + 4HCl$	1956	Munster et al.	/167/

Kelley /62/ considers the entropy values of gaseous $TiCl_4$ determined by Herman /158/ at high temperatures to be the most reliable. Values are presented in Table 154.

TABLE 154

Entropy of $TiCl_4$, cal/mole · deg /158/

T,°K	$S_T - S^\circ_{298}$	T,°K	$S_T - S^\circ_{298}$	T,°K	$S_T - S^\circ_{298}$
400	6.91	800	24.09	1400	38.37
500	12.34	900	27.08	1600	41.80
600	16.86	1000	29.76	1800	44.83
700	20.72	1200	34.42	2000	47.54

TABLE 155

Φ' function for $TiCl_4$ /133/

T, °K	Φ' cal/mole · deg	
	$TiCl_4$ (l)	$TiCl_4$ (g)
298	29.3	67.0
500	—	76.8
1000	—	92.0
1500	—	102.6

The Φ' function for $TiCl_4$. The Φ' functions for gaseous and liquid $TiCl_4$, calculated by Skinner and Ruehrwein /133/, are shown in Table 155.

Heat of formation of $TiCl_4$. The standard heats of formation of solid, liquid, and gaseous $TiCl_4$, according to various authors, is given in Table 156.

TABLE 156

Heat of formation of $TiCl_4$

Heat of formation $-\Delta H^\circ_{298}$, kcal/mole	Year	Author	Reference
		Solid $TiCl_4$	
196.4*	1955	Skinner, Ruehrwein	/133/
		Liquid $TiCl_4$	
185.0	1929	Roth, Bekker	/169/
192.9	1955	Skinner, Ruehrwein	/133/
192.5	1955	Farber, Darnell	/168/
190.3	1955	Gross et al.	/170/
192.1 ± 0.6	1956	Clifton, Macwood	/134/
190.0	1956	Krive et al.	/136/
191.2	1956	Altman et al.	/137/
		Gaseous $TiCl_4$	
182.6	1955	Skinner, Ruehrwein	/133/
183.0			
182.9	1955	Farber, Darnell	/168/
181.6	1956	Altman et al.	/137/

* At 0°K.

According to Gross et al. /170/, the heat of formation of liquid $TiCl_4$, according to the reaction $Ti(s) + 2Cl_2(l) = TiCl_4(l)$, is -181.49 kcal/mole.

For liquid $TiCl_4$, Bichowsky and Rossini /171/ give $\Delta H^\circ_{298} = 181.4$ kcal/mole. According to Kubaschewski and Evans /65/, the heat of formation of liquid $TiCl_4$ is given as $\Delta H^\circ_{298} = -183.0 \pm 2.5$ kcal/mole.

For the heat of formation of gaseous $TiCl_4$, the same authors /65/ give $\Delta H^\circ_{298} = -173.2 \pm 2.5$ kcal/mole.

For the heat of formation of liquid $TiCl_4$, Rossini and co-workers /32/ give $\Delta H^\circ_{298} = -179.3$ kcal/mole.

Free energy of formation of $TiCl_4$. For the free energy of formation of liquid $TiCl_4$, Rossini et al. /32/ give $\Delta F^\circ_{298} = -161.2$ kcal/mole.

The free energy of formation of liquid $TiCl_4$, according to the reaction $Ti(s) + 2Cl_2 = TiCl_2(l)$, and of gaseous $TiCl_4$, according to the reaction $Ti(s) + 2Cl_2 = TiCl_4(g)$, is expressed by the following equations, respectively.

$$\Delta F^\circ_T = -186{,}650 - 29.9\,T \log T + 140.6\,T$$

(±4 kcal/mole, 298 — 409°K)

$$\Delta F^\circ_T = -173{,}600 - 3.4\,T \log T + 39.5\,T$$

(±3.5 kcal/mole, 409 — 2000°K) /65/.

We present here thermodynamic data on $TiBr_2$, $TiBr_3$, and $TiBr_4$. For the first two compounds, Rossini and co-workers /32/ give the following heats of formation: $TiBr_2$, $\Delta H^\circ_{298} = 95$ kcal/mole; $TiBr_3$, $\Delta H^\circ_{298} = -132$ kcal/mole.

Titanium tetrabromide $TiBr_4$ ($M = 367.564$)

Crystal structure of $TiBr_4$. Titanium tetrabromide has a SnI_4 lattice. The lattice parameter a_0 is 11.25 Å /96/. Rolsten and Sisler /172/ found that $TiBr_4$ has a cubic crystal structure; the lattice parameter a_0 is 11.30 Å and there are eight $TiBr_4$ molecules per unit cell.

Allotropes of $TiBr_4$. Rossini and co-workers /32/ report the existence of two allotropes of $TiBr_4$. The α-form is stable up to $-15°$. At temperatures above $-15°$, the β-form exists.

Density of $TiBr_4$. According to Rolsten and Sisler /172/, the density of $TiBr_4$ is 3.383 g/cm^3. Luchinskii /17/ gives 3.31 g/cm^3.

Transition temperature of $TiBr_4$. The transition temperature of $TiBr_4$ is $-15°$ /32/.

Melting point of $TiBr_4$. According to Bond and Crone /173/, the melting point of $TiBr_4$ is 311.3°K. Luchinskii /17/ and Kubaschewski and Evans /65/ both give a melting point of 312.2°K. Rossini /32/ and co-workers give the melting point as 311.7°K.

Boiling point of $TiBr_4$. Hall et al. /174/ observed that at 1 atm $TiBr_4$ boils at 233.4° (506.6°K). A boiling point of 234° was determined by Kato and Abe /175/. Luchinskii /17/ and Rossini et al. /32/ give 230°, while Kubaschewski and Evans /65/ report that $TiBr_4$ boils at 222°.

Vapor pressure of $TiBr_4$. The vapor pressure of $TiBr_4$ was determined by Kato and Abe /175/ from 100 to 200°. Their data were found to fit the equation:

$$\log P\,(\text{mm Hg}) = -\frac{2501}{T} + 7.8083.$$

Hall and co-workers /174/ studied the vapor pressure of $TiBr_4$ and derived the following equation:

$$\log P\,(\text{atm}) = -\frac{3706.29}{T} - 6.2424 \log T + 24.199.$$

Ceki /176/ gives the following equations for the variation of the vapor pressure of $TiBr_4$ with absolute temperature:
for solid $TiBr_4$ from 298°K to the melting point

$$\log P\,(\text{mm Hg}) = -\frac{3260}{T} + 10.27$$

and for liquid $TiBr_4$ from the melting point to the boiling point

$$\log P\,(\text{mm Hg}) = -\frac{2580}{T} + 8.11.$$

Heat of fusion of $TiBr_4$. From their study of the system $TiBr_4$ — SO_2, Bond and Crone /173/ calculated a heat of fusion of $TiBr_4$ of 2060 cal/mole, but Kelley remarks that this value is not accurate.

Kubaschewski and Evans /65/ consider the most reliable value to be 3.1 ± 0.3 kcal/mole. Rossini et al. /32/ give the value 2.1 kcal/mole at 311.7°K.

Entropy of fusion of $TiBr_4$. According to Rossini et al. /32/, the entropy of fusion of $TiBr_4$ is given by ΔS_{fus} = 6.7 cal/mole · degree at 311.7°K.

Heat of vaporization of $TiBr_4$. The heat of vaporization of $TiBr_4$ was determined by Hall et al. /174/, Ceki /176/, and Kato and Abe /175/. According to Hall /174/, the heat of vaporization of $TiBr_4$ is 13.22 ± 0.10 kcal/mole and 10.60 ± 0.10 kcal/mole at 298°K and 506.6°K, respectively. Ceki /176/ gives L_{vap} = 11.3 ± 1.5 kcal/mole at the boiling point of $TiBr_4$. According to Kato and Abe /175/, L_{vap} = 11.44 kcal/mole at the same temperature.

Entropy of vaporization of $TiBr_4$. According to Hall and co-workers /174/, the entropy of vaporization of $TiBr_4$ is 27.58 ± 0.22 e.u. and 20.93 ± 0.22 e.u. at 298°K and 506.6°K, respectively.

Free energy of vaporization of $TiBr_4$. According to Kato and Abe /175/, the free energy of vaporization of $TiBr_4$ from 100 to 200° is expressed by the following equation:

$$\Delta F^{\circ}_{vap} = 11{,}445 - 35.73\,T \text{ cal/mole.}$$

Heat of sublimation of $TiBr_4$. The heat of sublimation of $TiBr_4$ was determined by Ceki /176/ as 16.7 ± 1.0 kcal/mole and 16.6 ± 1.0 kcal/mole at 25° and at the melting point of the compound, respectively.

Entropy of $TiBr_4$. From data on the entropy of vaporization of $TiBr_4$ and on the absolute entropy of $TiBr_4$ [g], Hall et al. /174/ calculated the standard entropy, S°_{298}, of solid titanium tetrabromide to be 57.6 ± 0.22 e.u.

The authors /174/ remark that their value is in good agreement with the value 57.2 ± 0.9 e.u. calculated from the heat capacity of solid $TiBr_4$ at low temperatures.

Heat of formation of $TiBr_4$. According to the experimental data of Süe /177/, the heat of formation of solid $TiBr_4$ is given by ΔH°_{298} = −150.0 ± 15.0 kcal/mole.

Schäfer and Schidtke /178/ determined the heat of formation of $TiBr_4$ by the calorimetric method and obtained the value ΔH°_{298} = −147.9 ± 0.3 kcal/mole.

For solid $TiBr_4$, Rossini and co-workers /32/ give ΔH°_{298} = −155 kcal/mole.

IODIDES OF TITANIUM

For the solid iodides of bivalent and trivalent titanium, Rossini and co-workers /32/ only report the heats of formation: ΔH°_{298} = −61 kcal/mole and ΔH°_{298} = −80 kcal/mole for TiI_2 and TiI_3, respectively.

Titanium tetraiodide TiI_4 (M = 555.58)

Crystal structure of TiI_4. Titanium tetraiodide has the SnI_4 type crystal structure with a lattice parameter a_0 of 12.00 Å /96/. At 125°, TiI_4 has a cubic lattice, a_0 = 12.21 Å, and there are eight molecules of TiI_4 per cell /172/.

Density of TiI_4. The density of TiI_4 is 4.01 g/cm^3 /172/.

Melting point of TiI_4. Kubaschewski and Evans /65/ and Rossini and co-workers /32/ both give the melting point of TiI_4 as 150°.

Boiling point of TiI_4. Luchinskii /17/ gives the boiling point of TiI_4 as 360°, while both Kubaschewski and Evans /65/ and Rossini and co-workers /32/ give 377°.

Vapor pressure of TiI_4. The vapor pressure of TiI_4 is 760 mm Hg at 377° (650.2°K).

According to Blocher and Campbell /179/, the vapor pressure of liquid TiI_4 (from 430 to 643°K) obeys the following equation:

$$\log P(\text{mm Hg}) = -\frac{3054}{T} + 7.576.$$

Heat of fusion of TiI_4. For the heat of fusion of TiI_4, Kubaschewski and Evans /65/ give $L_{fus} = 4.4 \pm 0.8$ kcal/mole.

Heat of vaporization of TiI_4. The heat of vaporization of this compound is given by $L_{vap} = 17.6 \pm 1.5$ kcal/mole at 25° and $L_{vap} = 13.4 \pm 1.5$ kcal/mole at the boiling point /65/. Rossini and co-workers /32/ give $L_{vap} = 13.6$ kcal/mole at 377.1°.

Entropy of vaporization of TiI_4. According to Rossini et al. /32/, the entropy of vaporization of TiI_4 is given by $\Delta S^\circ_{vap} = 20.9$ cal/mole · degree at 650.3°K and a pressure of 1 atmosphere.

Heat of sublimation of TiI_4. The heat of sublimation of TiI_4 is 21.6 ± 1.5 kcal/mole at 25° and 20.5 ± 1.5 kcal/mole at its melting point /65/.

Entropy of TiI_4. The standard entropy of TiI_4 is given by $S^\circ_{298} = 64.5 \pm 6.0$ cal/mole · degree /65/.

Heat of formation of TiI_4. Kubaschewski and Evans /65/ give $\Delta H^\circ_{298} = -85.0 \pm 10.0$ kcal/mole for the heat of formation of solid TiI_4; Rossini and co-workers /32/ give $\Delta H^\circ_{298} = -102.$ kcal/mole.

18. TITANIUM CARBIDE TiC ($M = 59.91$)

Crystal structure of TiC. Titanium carbide, TiC, has a NaCl type crystal structure /180/. Values for the crystal lattice parameters of TiC according to various authors are given in Table 157.

Density of TiC. According to Junker /189/, the density of TiC is 4.25 g/cm^3 at 20°. Luchinskii /17/ gives the value of 4.4 g/cm^3.

Melting point of TiC. The melting point of TiC as determined by Agte and Moers /190/ is 3410°K. Luchinskii /17/ reports 3160°(3433°K). According to Kubaschewski and Evans /65/, titanium carbide melts at 3150°K. Rossini et al. /32/ report 3400°K.

Boiling point of TiC. Kubaschewski and Evans /65/ give the boiling point of TiC as approximately 4300° (4578°K).

Heat capacity of TiC. The molar heat capacity of TiC from 55 to 295°K was determined by Kelley /71/. His results are presented below:

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity cal/mole · deg	0.00*	0.04*	0.23	1.75	3.76	5.57	8.04

* Extrapolated.

TABLE 157

Lattice parameters of TiC

Lattice parameter, in kX	Carbon content in TiC % (by weight)	Year	Author	Reference
4.29	Not known	1924	Van Arkel	/181/
4.60	"	1925	Becker, Ebert	/182/
4.310 ± 0.002	"	1931	Brantley	/183/
4.311	"	1932	Schwarz, Summa	/184/
4.3 — 4.32	18 — 20	1934	Burgers, Basart	/185/
4.31	48 — 50**	1940	Dawihl, Rix	/186/
4.317	19.32	1940	Meerson et al.	/187/
4.319	20.00	1949	Ehrlich	/188/
4.31*	—	1943	Laves	/180/

* Parameter expressed in Å.

** In at. %.

For solid TiC, Rossini et al. /32/ give C_P = 8.04 cal/mole·degree at 298°K.

According to Naylor /191/, the molar heat capacity of TiC is expressed by the following equation, valid from 298 to 1800°K:

$$C_P = 11.83 + 0.80 \cdot 10^{-3} T.$$

Heat content of TiC. The heat content of solid TiC as determined by Naylor /191/ is presented in Table 158.

TABLE 158

Heat content of solid TiC, cal/mole /191/

T, °K	$H_T^\circ - H_{298}^\circ$	T, °K	$H_T^\circ - H_{298}^\circ$	T, °K	$H_T^\circ - H_{298}^\circ$
400	945	900	6600	1400	12860
500	1975	1000	7830	1500	14130
600	3085	1100	9080	1600	15400
700	4225	1200	10330	1700	16670
800	5395	1300	11590	1800	17940

The data of Table 158 obey the following equation:

$$H_T - H_{298}^\circ = 11.83T + 0.40 \cdot 10^{-3}T^2 + 3.58 \cdot 10^5 T^{-1} - 4764,$$

valid from 298 to 1800°K. The accuracy of this equation is 0.5%.

Entropy of TiC. From his heat capacity data for solid TiC at 55 to 295°K, Kelley /71/ calculated the entropy of TiC: S_{50}° = 0.08 (extrapolated), $S_{298}^\circ - S_{50}^\circ$ = 5.71 (experimental), and S_{298}° = 5.79 ± 0.05 cal/mole · degree. Kubaschewski and Evans /65/, referring to the work of Kelley /71/, give S_{298}° = 5.2 ± 0.2 cal/mole · degree for the standard entropy of solid TiC. Rossini and co-workers /32/ give S_{298}° = 5.8 cal/mole.

The values of Naylor /191/ for the entropy of solid TiC at high temperatures are quoted in Table 159.

TABLE 159

Entropy of solid TiC in cal/mole · deg /191/

T, °K	$S_T^\circ - S_{298}^\circ$	T, °K	$S_T^\circ - S_{298}^\circ$	T, °K	$S_T^\circ - S_{298}^\circ$
400	2.72	900	11.77	1400	17.29
500	5.01	1000	13.07	1500	18.17
600	7.03	1100	14.26	1600	18.99
700	8.79	1200	15.35	1700	19.76
800	10.35	1300	16.35	1800	20.49

Heat of formation of TiC. Table 160 contains the heat of formation of solid TiC according to the reaction Ti (s) + C (s) = TiC (s).

TABLE 160

Heat of formation of TiC

Heat of formation $-\Delta H_{298}^\circ$ kcal/mole	Year	Author	Reference
57.25	1937	Kelley	/113/
57.0 ± 10.0	1943	Weibke, Kubaschewski	/192/
54.0	1952	Rossini et al.	/32/
57.2	1954	Kubaschewski, Evans	/65/

Free energy of formation of TiC. The free energy of formation of solid titanium carbide is given by $\Delta F_{298}^\circ = -53$ kcal/mole /14/.

Kelley /113/ derived the following equation for the variation of free energy of formation of solid TiC with absolute temperature:

$$\Delta F_T^\circ = -57{,}250 + 2.48T,$$

and calculated the value $\Delta F_{298}^\circ = -56.510$ cal/mole. Kubaschewski and Evans /65/ give the equation $\Delta F_T^\circ = -57{,}000 + 2.75T$, which is suitable for the calculation of the free energy of formation of solid TiC from 298 to 2000°K. The accuracy of this equation is ±10 kcal/mole.

19. TITANIUM NITRIDE TiN (M = 61.908)

Crystal structure of TiN. Titanium nitride has a NaCl type cubic crystal structure; with the lattice parameter $a_0 = 4.23$ /75, 79/. The compound δ-TiN (22.65% N) has an hexagonal crystal lattice and the same parameter /194/.

Density and molar volume of TiN. The density of TiN, as determined by various authors, is given in Table 161.

According to Herzer /196/, the molar volume of TiN is 12.1 cm^3/mole. Kubaschewski and Hopkins /79/ give 11.4 to 11.8 cm^3/mole.

Melting point of TiN. According to Friedrich and Sittig /107/, the melting point of TiN is 2927°. Agte and Moers /190/ and Pollard and Woodword /194/ determined the values 3220±50°K and 2950±50°, respectively.

Rossini et al. /32/ give 2927°, Kubaschewski and Evans /65/ 2940°, and Luchinskii /17/ 2990°.

Heat capacity of TiN. The heat capacity of solid TiN at low temperatures according to /71/ is presented below:

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity, cal/mole · deg.	0.00*	0.06*	0.44	2.57	4.75	6.54	8.86

A heat capacity of 8.86 cal/mole · degree at 298°K is given by Rossini and co-workers /32/. Pollard and Woodword /194/ give 11.91 cal/mole · degree at 298°K.

TABLE 161

Density of TiN

Temperature, °C	Density g/cm^3	Year	Author	Reference
18	5.10	1908	Ruff, Eisner	/195/
—	5.18	1925	Friedrich, Sittig	/107/
20	5.122	1927	Herzer	/196/
18	5.16	1941	Luchinskii	/17/
—	4.87*	1949	Ehrlich	/197/
—	5.24			
—	5.44**	1950	Pollard	/194/
—	5.21†			

* Refers to $TiN_{0.44}$.

** Calculated for δ-TiN (22.65% N).

† Experimental data for δ-TiN (22.65 %N).

According to Naylor /78/, the heat capacity of solid TiN is given by the equation:

$$C_p = 11.91 + 0.94 \cdot 10^{-3} T - 3.58 \cdot 10^5 \cdot T^{-2}.$$

This equation is valid from 298 to 1800°K. Its accuracy is 1%.

Heat of fusion of TiN. The heat of fusion of solid TiN is approximately 20.0 kcal/mole /11/.

Heat of combustion of TiN. The heat of combustion of this compound was determined by Naylor /78/ and found to be 144.9±0.1 kcal/mole at 19°.

Heat of decomposition of TiN. Hoch et al. /202/ studied the vapor formation of TiN from 1987 to 2241°K, using the Knudsen effusion method. They found that TiN decomposes into gaseous titanium and nitrogen and that the heat change accompanying this process is 191.2 kcal/mole at 0°K. According to Kubaschewski and Hopkins /79/, the heat of decomposition of TiN is 160.6 kcal/mole at 25°.

Free energy of decomposition of TiN. Kubaschewski and Hopkins /79/ give $\Delta F^{\circ}_{298} = 73.5$ kcal/mole for the free energy of decomposition.

Heat content of TiN. Kelley /62/, referring to the work of Naylor /78/ and Kato and Abe /175/, reports the following values for the heat content of TiN (Table 162).

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* Extrapolated.

The data of Table 162 obey the equation

$$H_T - H^\circ_{298} = 11.91T + 0.47 \cdot 10^{-3}T + 2.96 \cdot 10^5 T^{-1} - 4586,$$

valid from 298 to 1800°K. The accuracy of this equation is 0.5%.

TABLE 162

Heat content of TiN /78, 62, 175/

T, °K	$H_T - H^\circ_{298}$ kcal/mole	T, °K	$H_T - H^\circ_{298}$ kcal/mole	T, °K	$H_T - H^\circ_{298}$ kcal/mole
400	1000	900	6810	1400	13230
500	2090	1000	8050	1500	14550
600	3230	1100	9310	1600	15870
700	4400	1200	10600	1700	17190
800	5590	1300	11910	1800	18510

Entropy of TiN. According to Neumann and co-workers /200/, the entropy of solid TiN is given by $S^\circ_{298} = 8.5$ cal/mole · degree. From Shomate's heat capacity data /112/ for solid TiN from 52 to 297°K, Kelley calculated the entropies: $S^\circ_{298} = 0.17$ (extrapolated), $S^\circ_{298} - S^\circ_{52} = 7.07$ (experimental), and $S^\circ_{298} = 7.24 \pm 0.04$ cal/mole · degree. Kubaschewski and Evans /65/ quote the entropy of solid TiN given by Shomate /112/: $S^\circ_{298} = 7.2 \pm 0.4$ cal/mole · degree. The same entropy is given by Rossini et al. /32/.

The entropy of solid TiN from 400 to 1800°K is given in given in Table 163 /62/.

TABLE 163

Entropy of solid TiN

T, °K	$S^\circ_T - S^\circ_{298}$ cal/mole·deg	T, °K	$S^\circ_T - S^\circ_{298}$ cal/mole·deg	T, °K	$S^\circ_T - S^\circ_{298}$ cal/mole·deg
400	2.88	900	12.21	1400	17.87
500	5.31	1000	13.52	1500	18.78
600	7.39	1100	14.72	1600	19.63
700	9.19	1200	15.84	1700	20.43
800	10.78	1300	16.89	1800	21.19

Heat of formation of TiN. The heat of formation of solid TiN from its elements is given by $\Delta H^0_{298} = -80.3$ and $\Delta H^0_{273} = -80.5$ kcal/mole, according to Neumann et al. /200/ and Humphrey /201/, respectively. Weibke and Kubaschewski /203/ give $\Delta H^0_{298} = -80.3 \pm 2.0$ kcal/mole.

For the heat of formation of solid TiN, Rossini and co-workers /32/ give $\Delta H^0_{298} = -73.0$ kcal/mole.

Entropy of formation of TiN. According to Mah and Gellert /204/, the entropy of formation of solid TiN is given by $\Delta S^0_{298} = -22.3$ e.u. Kelley /113/ gives $\Delta S^0_{298} = -21.0$ cal/mole · degree.

Free energy of formation of TiN. The free energy of formation of solid TiN is given by $\Delta F^0_{298} = -66.1$ kcal/mole /32/ and $\Delta F^0_{273} = -7.37$ kcal/mole /20/.

According to Kelley /113/, the free energy of formation of solid TiN is given by the equation $\Delta F^\circ_T = -80{,}300 + 21T$, from which $\Delta F^0_{298} = -74{,}040$ kcal/mole was calculated.

The free energy of formation (1800 to 2100°K) of solid TiN was also determined by Naylor /78/, who gives the equation $\Delta F_T^\circ = 80{,}250 - 22.85T$.

Kubaschewski and Evans /65/ give the following equation for the free energy of formation of TiN according to the reaction $Ti(s) + {}^1/_2N_2 = TiN(s)$

$$\Delta F_T^\circ = -80{,}300 + 22.85T.$$

This equation is valid from 298 to 2000°K and its accuracy is ±6 kcal/mole.

20. DIRECT REDUCTION, OXIDATION, AND CHLORINATION REACTIONS

Reduction of TiO_2 by hydrogen

The reduction of TiO_2 by hydrogen from 1022 to 1282°K was studied by Nazu /205/, who used a dynamic method. By measuring the loss in weight of titanium oxide samples, this author determined that the reduction of TiO_2 results in formation of a compound of the formula $Ti_2O_{3,05}$. For the simple reaction $2TiO_2 + H_2 \rightleftharpoons Ti_2O_3 + H_2O$, from 1022 to 1282°K, Nazu /205/ determined the mean equilibrium constant values $K_p = \frac{P_{H_2O}}{P_{H_2}}$, presented in Table 164.

TABLE 164

Mean equilibrium constants for reaction $2TiO_2 + H_2 \rightleftarrows Ti_2O_3 + H_2O$ /205/

T, °K	$\frac{1}{T}$	K_p	log K_p	T, °K	$\frac{1}{T}$	K_p	log K_p
1022 ± 1	0.000978	0.176	−0.75449	1178 ± 2	0.000849	0.432	−0.36452
1074 ± 2	0.000931	0.220	−0.65758	1230 ± 2	0.000813	0.475	−0.32330
1126 ± 1	0.000888	0.320	−0.51999	1282 ± 2	0.000780	0.595	−0.22548

Variation of the equilibrium constant with temperature is given by the following logarithmic equation:

$$\log K_p = 1.9305 - \frac{2754}{T}.$$

This author also derived an equation for the heat of reduction of TiO_2 with hydrogen:

$$\Delta H_T^\circ = 4095 + 0.874T + 0.003856T^2,$$

from which $\Delta H_{298}^0 = 4700$ cal/mole.

The entropy of reduction of TiO_2 with hydrogen was also calculated by Nazu /205/. He gave $\Delta S_{298}^0 = 1.95$ cal/mole · degree. The free energy of the reduction of TiO_2 by hydrogen obeys the following equation /205/:

$$\Delta F_T^\circ = 4095 - 2.0125 \cdot T \log T - 0.003856T^2 + 10.1T,$$

from which $\Delta F_{298}^0 = 5280$ cal/mole.

Belyakova and co-workers /206/ studied the reduction of TiO_2 with hydrogen from 1200 to 1500°. They found that this reduction proceeds to Ti_2O_3. At 1500° however, in addition to the main product, a certain amount of titanium monoxide may also be formed.

Reduction of TiO_2 by carbon monoxide

The reduction of TiO_2 by carbon monoxide, according to the reaction $2TiO_2 + CO = Ti_2O_3 + CO_2$ (I), was studied by Nazu /205/.

He calculated the standard free energy of reaction (I) from equation:

$$\Delta F_T^\circ = -6005 - 2.1552\,T \log T - 0.0_2 8306 T^2 - 0.0_6 68 T^3 + 10.64\,T,$$

from which $\Delta F_{298}^\circ = -6220$ cal/mole.

Reduction of TiO_2 by carbon

The reduction of TiO_2 by carbon proceeds according to the reaction $TiO_2 + 3C = TiC + 2CO$.

It was studied by Brantley and Beckman /209/. The reactants were placed in an electrically heated graphite tube furnace and the pressure of CO was determined. Experimental results are presented in Table 165.

TABLE 165

Variation of the coequilibrium pressure and free energy of reaction $TiO_2 + 3C = TiC + 2CO$ with temperature /205/

T, °K	$\frac{1}{T}10^4$	P_{CO}, atm.	log P	Free energy ΔF_T° cal/mole
1278	7.825	0.796	−0.0991	+1158
1323	7.559	1.081	+0.0338	−409
1324	7.553	1.114	+0.0469	−568
1349	7.413	1.216	+0.0849	−1047
1386	7.215	1.634	+0.2133	−2703
1428	7.003	1.995	+0.2999	−3916

X-ray analysis of the solid phase confirmed the presence of TiO_2, C, and TiC.

Variation of log P with the reciprocal of the absolute temperature is given by the following equation:

$$\log P\,(\text{atm}) = -\frac{5024}{T} + 3.829 \quad (1278 \text{ to } 1428°\text{K}).$$

The equilibrium pressure of CO, as calculated from the above equation, is 1 atm. at 1312°K.

The free energy of reaction (I) from 1278 to 1428°K, calculated from the equation $\Delta F_T^\circ = -RT\ln K_p$ (where $K_p = P_{CO}^2$), is given by $\Delta F_T^\circ = 45{,}930 - 35.01\,T$.

Kelley /113/ is critical of the data of Brantley and Beckman /209/. He has nevertheless used their results for the reaction $TiO_2 + 3C = TiC + 2CO$ to derive the following equations:

$$\Delta H_T^\circ = 109{,}400 - 4\,T,$$

from which

$$\Delta H^{\circ}_{298} = 108{,}210 \text{ cal/mole}$$

and $$\Delta F^{\circ}_{T} = 109{,}400 + 9.2\,T\log T - 110.86T,$$

from which

$$\Delta F^{\circ}_{298} = 83{,}140 \text{ cal/mole}.$$

The reduction of TiO_2 was also studied by Belyakova et al. /206/, Meerson and Lipkes /210/, Samsonov /211/, Meerson and Krein /212/.

Belyakova and co-workers report /206/ that reduction of TiO_2 with charcoal at 1100 to 1500° results in formation of a solid solution of TiC and TiO, containing from 33 to 60% TiC.

Meerson and Lipkes /210/ studied the formation of titanium carbide according to the reaction $TiO_2 + C = TiC + CO_2$. They showed that reduction of titanium dioxide by carbon with resultant formation of the carbide proceeds in three stages, described by the following equations:

$$2TiO_2 + C \rightleftharpoons Ti_2O_3 + CO,$$

$$Ti_2O_3 + C \rightleftharpoons 2TiO + CO,$$

$$TiO + 2C \rightleftharpoons TiC + CO.$$

The thermodynamic data of Brantley and Beckman /209/ are therefore wrongly based on the reaction $TiO_2 + 3C \rightleftharpoons TiC + 2CO$ and Kelley's calculations above /113/, based on their results, are invalid.

Furthermore, we know from our own experience and that of other workers that even at temperatures as high as 2000° the reaction $TiO_2 + 3C = TiC + 2CO$ does not proceed to completion, owing to formation of solid solutions of TiO—TiC. Brantley and Beckman /209/ nevertheless based their calculations on the supposition that equilibrium is reached at a temperature as low as 1040°.

The last stage of the formation of titanium carbide by reduction of TiO_2 with carbon was exhaustively studied by Meerson and Krein /212/. These authors found that when titanium carbide is produced in vacuo the last stage, depending on the conditions, proceeds with simultaneous formation of the solid solutions TiO—TiC, TiO—TiC—Ti, or Ti—TiC, according to the reactions:

$$TiO + 2C \rightleftharpoons TiC + CO;$$

$$TiO + C \rightleftharpoons Ti + CO;$$

$$Ti + C \rightleftharpoons TiC.$$

At CO pressures above 100 mm Hg carburization of titanium takes place according to the reaction $TiO + 2C \rightleftharpoons TiC + CO$, and CO plays the role of an oxidizing agent. A further decrease of CO pressure causes the partial removal of oxygen from solid solution and reduction of titanium, which enters the solid solution TiC — TiO — Ti in place of the oxygen which has been removed. For CO pressures below 10 mm Hg and temperatures above 1300°, oxygen is removed completely; the decrease in pressure of CO causes the carbide to lose a part of its carbon, according to the reaction $TiC + CO_2 \rightleftharpoons Ti + 2CO$.

Reduction of TiO_2 by calcium.

Titanium dioxide can be reduced by metallic calcium according to the reaction $TiO_2 + 2Ca \rightleftharpoons Ti + 2CaO$.

In order that the reaction should proceed to the right, it is necessary to use 1.2 to 3.0 times as much calcium as titanium dioxide /213/.

Oxidation of Ti_2O_3 by oxygen

According to Nazu /205/, the heat and free energy of the reaction $\frac{1}{2}Ti_2O_3 + \frac{1}{2}O_2 = TiO_2$ are given by the following equations:

$$\Delta H_T^\circ = -61{,}520 - 1.814T - 0.0_25506T^2 - 0.0_674T^3,$$

$$\Delta F_T^\circ = -61{,}520 + 4.1769T \log T + 0.0_25506T + 0.0_637T^3 - 6.13T.$$

At 25° the heat and free energy of the above reaction are as follows:

$$\Delta H_{298}^\circ = -62{,}530 \text{ cal/mole and } \Delta F_{298}^\circ = -59{,}770 \text{ cal/mole.}$$

Junker /214/, using the Nernst equation, calculated the heat of oxidation of Ti_2O_3 with oxygen according to the reaction $\frac{1}{2}Ti_2O_3 + \frac{1}{2}O_2 = TiO_2$, and obtained $\Delta H = -99{,}000$ cal/mole.

Action of chlorine on TiO_2

Kangro and Jahn /215/ studied the action of chlorine on titanium dioxide at high temperatures under the following conditions: flow rate of chlorine 15 l/hour, duration of experiment 1 hour. They consider the action of chlorine appreciable, when 1% of TiO_2 is converted to titanium chloride. Appreciable action of gaseous chlorine therefore begins at 800°, the final product being titanium tetrachloride:

$$TiO_2\,(s) + 2Cl_2 = TiCl_4 + O_2. \qquad \text{(II)}$$

Pamfilov and co-workers /216/ showed that the optimum temperature for chlorination of TiO_2 in the presence of a MnO_2 catalyst is between 400 and 420°. Their experiments /216/ confirmed the reaction suggested by Kangro and Jahn /215/: $TiO_2 + 2Cl_2 = TiCl_4 + O_2$. It seems however that this is an overall reaction and proceeds via several intermediate reactions.

Action of chlorine on TiO_2 in the presence of carbon

Godnev and Pamfilov /217/ report that gaseous $TiCl_4$, carbonyl chloride, and carbon dioxide are produced by the action of gaseous chlorine on a mixture of TiO_2 and carbon. The authors /217/ used the following reaction scheme to determine the partial pressures of gaseous components:

$$TiO_2\,(s) + 4Cl_2\,(g) + 2C\,(s) \rightleftharpoons TiCl_4\,(g) + 2COCl_2\,(g);$$

$$COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g);$$

$$2CO\,(g) \rightleftharpoons CO_2\,(g) + C\,(s).$$

The equilibrium constants K_p are given by

$$K_1 = \frac{P^4_{Cl_2}}{P_{TiCl_4} \cdot P^2_{COCl_2}},$$

$$K_2 = \frac{P_{COCl_2}}{P_{CO} \cdot P_{Cl_2}};$$

$$K_3 = \frac{P^2_{CO}}{P_{CO_2}}$$

and

$$2P_{TiCl_4} = P_{COCl_2} + P_{CO} + 2P_{CO_2}.$$

The sum of the partial pressures is given by

$$P = P_{Cl_2} + P_{TiCl_4} + P_{COCl_2} + P_{CO} + P_{CO_2}.$$

The authors /217/ also calculated the heat change for reaction (II), i. e., action of chlorine on TiO_2 in the presence of carbon, and obtained the value ΔH^0_{298} = 62.5 kcal/mole.

Values of the equilibrium constants, K_1, K_2, and K_3, from 400 to 1000°, were calculated by use of the Nernst approximation formula, and are given in Table 166.

TABLE 166

Mean values of the equilibrium constants K_1, K_2, and K_3 of chlorination of TiO_2 in the pressence of carbon /217/

t, °C	K_1	K_2	K_3
400	$0.425 \cdot 10^{-11}$	23.3	$0.538 \cdot 10^{-4}$
600	$0.303 \cdot 10^{-6}$	0.222	$0.830 \cdot 10^{-1}$
800	$0.361 \cdot 10^{-3}$	$0.11 \cdot 10^{-1}$	7.53
1000	$0.491 \cdot 10^{-1}$	$0.113 \cdot 10^{-2}$	160.4

From the equations for K_1, K_2, and K_3, the authors also determined graphically the partial equilibrium pressures of CO, CO_2, $TiCl_4$, $COCl_2$, and Cl_2 at 400 to 1000° and a total pressure of 1 atm. (Table 167).

TABLE 167

Partial pressures of components of the reaction between chlorine and TiO_2 in the presence of carbon /217/

t, °C	P_{CO}	P_{CO_2}	P_{TiCl_4}	P_{COCl_2}	P_{Cl_2}
400	0.0054	0 4346	0.500	$2.3 \cdot 10^{-8}$	$1.38 \cdot 10^{-7}$
600	0.175	0.370	0.455	$5.7 \cdot 10^{-7}$	$1.47 \cdot 10^{-5}$
800	0.600	0.047	0.353	$4.9 \cdot 10^{-7}$	$7.4 \cdot 10^{-5}$
1000	0.6623	0.0027	0.335	$9.9\ 10^{-8}$	$1.12 \cdot 10^{-4}$

At the equilibrium point the gaseous phase consists mainly of $TiCl_4$, CO, and Cl_2. With increasing temperature the concentration of CO increases and that of CO_2 decreases.

At lower temperatures the following overall reaction occurs:

$$TiO_2\,(s) + 2Cl_2\,(g) + C\,(s) = TiCl_4\,(g) + CO_2\,(g).$$

At temperatures of about 1000°, the reaction occurs as follows:

$$TiO_2\,(s) + 2Cl_2\,(g) + 2C\,(s) \rightleftharpoons TiCl_4\,(s) + 2CO\,(g).$$

This reaction has been verified from gas analysis data obtained by Pamfilov and Shtandel' /218/.

Action of chlorine on TiO_2 in the presence of carbon monoxide

Pamfilov and Shikher /219/ studied the chlorination of solid TiO_2 with a mixture of gaseous chlorine and carbon monoxide at temperatures of 227 to 1227°. They gave the following overall reaction:

$$TiO_2\,(s) + 2Cl_2\,(g) + 2CO\,(g) \rightleftharpoons TiCl_4\,(g) + 2CO_2\,(g), \qquad (III)$$

with an equilibrium constant

$$K_p = \frac{P^2_{Cl_2} \cdot P^2_{CO}}{P_{TiCl_4} \cdot P^2_{CO_2}}.$$

Reaction (III) may be represented as the sum of the following reactions:

$$TiO_2\,(s) + 2Cl_2\,(g) \rightleftharpoons TiCl_4\,(g) + O_2\,(g);$$

$$2CO\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g),$$

where

$$K_1 = \frac{P^2_{Cl_2}}{P_{TiCl_4} \cdot P_{O_2}};$$

$$K_2 = \frac{P^2_{CO} \cdot P_{O_2}}{P^2_{CO_2}};$$

$$K = K_1 \cdot K_2 = \frac{P^2_{Cl_2} \cdot P^2_{CO}}{P_{TiCl} \cdot P^2_{CO_2}}.$$

Values of K_1 and K_2 from 227 to 1227°, as calculated by Pamfilov and Shikher /219/, according to the Nernst approximation formula, are given in Table 168.

TABLE 168

Mean values of equilibrium constants K_1, K_2, and K_3 for the reaction of chlorine on TiO_2 in the presence of carbon monoxide /219/

t, °C	K_1	K_2	K_3
227	$1.459 \cdot 10^{19}$	$7.261 \cdot 10^{-51}$	$1.059 \cdot 10^{-31}$
427	$6.472 \cdot 10^{13}$	$7.621 \cdot 10^{-34}$	$4.932 \cdot 10^{-20}$
627	$6.887 \cdot 10^{10}$	$2.254 \cdot 10^{-24}$	$1.552 \cdot 10^{-13}$
827	$8.800 \cdot 10^{8}$	$2.286 \cdot 10^{-18}$	$2.014 \cdot 10^{-9}$
1027	$4.315 \cdot 10^{7}$	$3.192 \cdot 10^{-14}$	$1.377 \cdot 10^{-6}$
1227	$4.732 \cdot 10^{6}$	$3.389 \cdot 10^{-11}$	$1.603 \cdot 10^{-4}$

The equilibrium partial pressures of $TiCl_4$, CO_2, and Cl_2 produced by the action of chlorine on TiO_2, in the presence of carbon monoxide at 227 to 1227° and a total pressure of 1 atm., are given in Table 169.

TABLE 169

Partial pressures of the components of the reaction between chlorine and TiO_2 in the presence of carbon monoxide /119/

t, °C	P_{TiCl_4}	P_{CO_2}	$P_{CO_2} = P_{CO}$	t, °C	P_{TiCl_4}	P_{CO_2}	$P_{CO_2} = P_{CO}$
227	0.33	0.66	$11 \cdot 10^{-8}$	827	0.33	0.66	$4.0 \cdot 10^{-3}$
427	0.33	0.66	$9.0 \cdot 10^{-6}$	1027	0.32	0.64	$1.7 \cdot 10^{-2}$
627	0.33	0.66	$3.7 \cdot 10^{-4}$	1227	0.29	0.58	$6.3 \cdot 10^{-2}$

Chapter 4

*THERMODYNAMIC PROPERTIES OF ZIRCONIUM AND OF ITS MORE IMPORTANT COMPOUNDS**

21. METALLIC ZIRCONIUM (M = 91.21)

Crystal structure, density, melting point, boiling point, vapor pressure

Allotropy of zirconium. Metallic zirconium, like titanium, exists in two allotropic modifications. The first, the α-form, is stable up to 862°, while the second, the β-form, is stable at temperatures above 862°. Komar /1/ observed by means of an electron gun that when zirconium is heated above 862° the β-modification is formed. It converts to a single crystallite on cooling.

The $\alpha \rightarrow \beta$-transition is not always reversible. When the temperature is repeatedly elevated, a cubic crystal sometimes forms with a different orientation from that of the original crystal. Whatever the crystal orientation however, the data established by Burgers /2/ by means of X-ray analysis are still valid.

The transition of zirconium from its α- to β-modification was first observed by Zwikker /3/. Vogel and Tonn /4/ determined the transition temperature by thermal analysis and obtained the value 862 ± 5°. Burgers /2/ gives 863 ± 3°, and Kubaschewski and Evans /16/ 852°.

Crystal structure of zirconium. The α-modification has the space group D_{6L}^4 (hexagonal close packing), the β-modification has the O_h^9 space group (body-centered cubic packing) /2/.

The lattice parameters at 25° for α-zirconium with a coordination number of 6.6 /5/ are as follows: a_0 = 3.230 ± 0.002 Å; c_0 = 5.133 ± 0.003 Å; c_0/a_0 = 1.589.

Later research /6/ gave the following data for α-zirconium: a_0 = 3.23 Å; c_0 = 5.14 Å; c_0/a_0 = 1.59.

Sof'ina et al. /6/ give a coordination number of 8 for β-zirconium and the parameter a_0 = 3.62 Å at 900°.

Density of zirconium. According to Adenstadt /7/, metallic hafnium-free zirconium has a density of 6.49 ± 0.001 g/cm^3. Boulger /8/ reports that a 2.5% hafnium content increases the density of zirconium to 6.52 g/cm^3.

Treco /9/, using X-ray analysis, studied the density of zirconium produced by different technological processes (g/cm^3):

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* Calculations of the thermodynamic properties of zirconium were carried out by S. I. Gorbov.

Iodide zirconium, oxygen-free	6.507
Iodide zirconium with low hafnium contents	6.504
Sponge zirconium produced by thermal reduction with magnesium	6.489
Iodide zirconium with high hafnium contents	6.574
Zirconium produced by thermal reduction with magnesium and melted in graphite	6.605

Coefficient of thermal expansion of zirconium. The coefficient of linear thermal expansion of zirconium at room temperature is $5.2 \pm 0.6 \cdot 10^{-6}$ degree^{-1} (Burgers /10/).

Kroll /11/ states that the coefficient of linear expansion of zirconium increases with increasing temperature (Table 170).

TABLE 170

Variation of the coefficient of linear expansion of zirconium with temperature /11/

t, °C	Coefficient of linear expansion $\alpha \times 10^6$, deg $^{-1}$
20—200	5.4
200--300	6.4
300—400	6.9
400—500	7.9
500—600	8.4
600—700	8.9

Note. The values of α at all temperatures are probably 1.8 to 3% too high.

McGeary and Lustman /12/ give the coefficients of linear expansion from −183 to 871° for hafnium-free zirconium annealed at 1000°K. Their values are presented below:

Temperature, °C	−183	−70	204	316	538
$\alpha \times 10^6$, deg $^{-1}$	−5.66	−5.88	6.23	6.23	6.10

The coefficient of linear expansion has various values, depending on whether it is determined in the direction parallel or perpendicular to the C axis of the crystal.

Russell /13/ found the following coefficients of linear expansion of zirconium at 25°:

$6.15 \cdot 10^{-6}$ degree^{-1} ($\parallel$ to the C axis),

$5.69 \cdot 10^{-6}$ degree^{-1} ($\perp$ to the C axis).

These values were determined with an accuracy of ±0.01%.

Zirconium, whose crystals have a non-uniform orientation, has a coefficient of linear expansion of $5.85 \cdot 10^{-6}$ degree^{-1} at 25°.

Figure 3 shows the mean coefficient of linear expansion of α-zirconium as a function of temperature. This coefficient was determined at low temperatures by Ereling /14/, at high temperatures by Russell /13/.

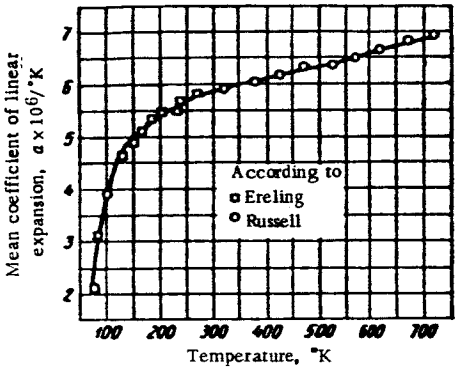

FIGURE 3. Mean values of the coefficient of linear expansion of zirconium as function of temperature (Russell and Ereling)

Melting point of zirconium. According to Burgers /10/, the melting point of zirconium containing impurities of hafnium is 1830 ± 40°. That of hafnium-free zirconium, according to Adenstadt /7/, is 1845°. Deardorff and Haynes /15/ report that they determined the melting point of of zirconium accurately as 1855 ± 15°. The reproducibility of their results was within ±3°. Kubaschewski and Evans /16/ give 1852°.

Vapor pressure of zirconium. "The Chemistry and Metallurgy of Miscellaneous Materials" /17/ edited by Quill contains the following rounded-off values for the vapor pressure of zirconium from 2450 to 3850°K:

Temperature, °K	2450	2700	3000	3850
Partial pressure, atm.	10^{-4}	10^{-3}	10^{-2}	1

Skinner et al. /18/ derived the following equation for the vapor pressure of zirconium:

$$\log P(\text{atm}) = -\frac{31066}{T} + 7.3351 - 2.415 \cdot 10^{-4} T.$$

Boiling point of zirconium. According to Quill /17/, the boiling point of zirconium is 3577°.

Heat capacity, heat of fusion, and heat of vaporization

Heat capacity of zirconium. According to Burgers /10/ and Squire and Kaufmann /19/, the specific heat capacity of zirconium is 0.067 ± 0.001 cal/g · degree at room temperature.

Adenstadt /7/ reports that the specific heat capacity of hafnium-free zirconium is 0.0693 cal/g · degree from 25 to 100°.

The specific heat capacity of zirconium as a function of temperature was studied by Squire and Kaufmann /19/. Their results are plotted in Figure 4.

The atomic heat capacities of zirconium determined by Boulger /8/ and by Todd /20/ show a difference of 1%. Todd showed that the 1% increase in the atomic heat capacity of zirconium was caused by impurities of hafnium. His values for the atomic heat capacities of zirconium (m. w. 91.22) are shown in Table 171.

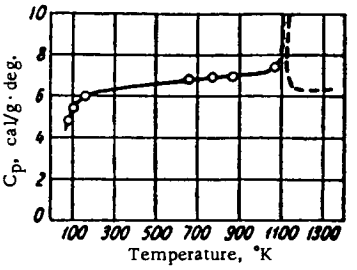

FIGURE 4. Variation of the specific heat capacity of zirconium with temperature

TABLE 171

Atomic heat capacity of solid zirconium /8, 20/

T, °K	C_P cal/g·atom·deg	T, °K	C_P cal/g·atom·deg	T, °K	C_P cal/g·atom·deg
53.2	2.408	115.0	4.796	216.4	5.861
56.8	2.640	124.1	4.971	226.2	5.905
60.8	2.873	135.1	5.172	236.4	5.948
65.6	3.134	146.2	5.293	246.0	5.981
70.6	3.383	156.0	5.409	256.7	6.024
75.4	3.609	166.1	5.510	266.4	6.083
79.8	3.789	176.0	5.606	276.4	6.127
84.1	3.945	186.2	5.672	286.6	6.149
94.9	4.296	196.1	5.737	296.8	6.168
104.5	4.562	206.3	5.802	298.16	6.186

Kolsky and Gilles /21/ give the atomic heat capacity of gaseous zirconium at various temperatures as follows:

T, °K	10	100	298.16	1000	3000	8000
C_P^*, cal/g·atom·deg	4.96798	5.01913	6.36770	6.12090	7.75086	9.31083

Todd /20/ also published data on the molar heat capacity of zirconium. These data were corrected for a 2.15% content (by weight) of Hf. Skinner and Johnston /93/ measured the heat capacity from 14 to 300°K of hydrogen-free zirconium of a higher degree of purity.

Their sample contained the following amounts of impurities (in at. %): 0.025 Hf; 0.67 Fe; 0.15 C; 0.026 N_2; 0.082 other impurities. Their results are presented in Table 172.

According to Kelley /22/, the atomic heat capacity (in cal/g·atom·degree) is given by the following equation:

$$C_p = 4.26 + 4.14 \cdot 10^{-3} T + 0.56 \cdot 10^5 T^{-2},$$

* Heat capacities at intermediate temperatures will be presented in the table of thermodynamic properties at the end of this chapter.

valid from 298 to 900°K. The heat capacity C_P calculated by this equation has the following values:

Temperature, °C	25	200	400	600
C_P, cal/g·atom·deg	6.122	6.47	7.163	8.596

Rutkowski /23/ derived the following formula,

$$C_P = 5.17 + 6.239 \cdot 10^{-3} T - 1.621 \cdot 10^{5} T^{-2},$$

which can be used up to 500°K.

If C_P is calculated according to this formula, it has the following values:

T, °C	25	200	400
C_P, cal/g·atom·deg	5.24	7.4	9.37

TABLE 172

Atomic heat capacities of solid zirconium (Skinner and Johnston /93/)

T, °K	C_P cal/g·atom·deg	T, °K	C_P cal/g·atom·deg	T, °K	C_P cal/g·atom·deg
14	0.09	125	4.986	250	5.918
25	0.489	150	5.299	275	5.981
50	2.212	175	5.525	298.16	6.012
75	3.609	200	5.691	300	6.014
100	4.46	225	5.824		

King and Coughlin /24/ give the following two equations for the atomic heat capacity of zirconium:
for α-zirconium (298 to 1135°K)

$$C_P = 6.83 + 1.12 \cdot 10^{-3} T - 0.87 \cdot 10^{5} T^{-2},$$

and $C_P = 7.27$ for β-zirconium (1135 to 1400°K). Using the first equation, the following values were obtained:

T, °C	25	500	800
C_P, cal/g·atom·deg	6.706	7.537	7.95

The accuracy of the first and second equation is 2%.

For metallurgical calculations the best equation is that of Kelley /22/.

In a more recent work Burk and co-workers /25/ measured and calculated the atomic heat capacities of zirconium from 20 to 200°K. Their results are given in Table 173.

Heat of transition of zirconium. King and Coughlin /24/ determined the heat of transition of zirconium at 625° and found $L_{trans} = 0.92 \pm 0.1$ kcal/mole.

Heat of fusion of zirconium. Kubaschewski and Evans /16/ give the following value for the heat of fusion of zirconium:

$$L_{fus} = 4.8 \pm 2.5 \text{ kcal/g} \cdot \text{atom}.$$

Quill /17/ gives 5.5 kcal/g·atom, but according to Miller, this value is rather doubtful.

Heat of vaporization of zirconium. Quill /17/ and Skinner et al. /18/ give the latent heat of vaporization as 120 kcal/mole and 142.15 ± 0.35 kcal/g·atom, respectively.

TABLE 173

Heat capacity of zirconium /25/

T, °K	C_p cal/g·atom·deg	C_v cal/g·atom·deg	T, °K	C_p cal/g·atom·deg	C_v cal/g·atom·deg	T, °K	C_p cal/g·atom·deg	C_v cal/g·atom·deg
20	0.2441	0.2441	85	4.028	—	145	5.240	—
25	0.4836	0.4836	90	4.202	4.199	150	5.305	—
30	0.7888	0.7888	95	4.352	—	155	5.376	—
35	1.136	1.136	100	4.498	4.494	160	5.447	5.437
40	1.502	1.502	105	4.610	—	165	5.517	—
45	1.850	1.805	110	4.709	4.704	170	5.573	—
50	2.183	2.182	115	4.808	—	175	5.625	—
55	2.512	2.511	120	4.892	4.887	180	5.667	5.656
60	2.822	2.821	125	4.972	—	185	5.695	—
65	3.103	3.102	130	5.038	—	190	5.714	—
70	3.371	3.370	135	5.103	—	195	5.737	—
75	3.610	—	140	5.174	5.467	200	5.751	5.733
80	3.831	3.829						

Note. Up to 100°K, the accuracy of the determination is ± 1%. At temperatures higher than 100°K, the accuracy is ± 5%.

Heat content and entropy of zirconium. The Φ' and Φ'' functions.

Heat content of zirconium. King and Coughlin /24/, using the experimental heat capacity curve, calculated the heat content of solid zirconium from the expression $H_T - H_0^0 = \int_0^T C_P dT$. Their results are shown in Table 174.

TABLE 174

Heat content of solid zirconium /24/

T, °K	$H_T - H_{298}^0$ cal/g·atom	T, °K	$H_T - H_{298}^0$ cal/g·atom	T, °K	$H_T - H_{298}^0$ cal/g·atom
390.3	605	968.5	4845	1165.8	7115
400	665	1000	5095	1182.1	7355
477.5	1195	1073.7	5680	1200	7560
500	1350	1082.0	5795	1208.3	7620
585.6	1970	1098.4	5855	1231.1	7790
600	2065	1100	5890	1253.0	7940
694.6	2775	1104.4	5925	1294.0	8260
700	2800	1124.7	6160	1300	8290
780.4	3400	1135 (α)	6170	1335.0	8530
800	3550	1135 (β)	7090	1371.0	8925
877.3	4140	1147.5	6685	1400	9015
900	4315				

The heat content from experimental data on the heat capacity of solid zirconium from 14 to 300°K (Table 175) was also calculated by Skinner and Johnston /93/.

TABLE 175

Heat content of zirconium according to Skinner and Johnston /93/

T, °K	$H_T - H_0^0$ cal/g·atom	T, °K	$H_T - H_0^0$ cal/g·atom	T, °K	$H_T - H_0^0$ cal/g·atom
14	0.31	125	330.5	250	1025.6
25	3.16	150	459.3	275	1174.5
50	36.0	175	594.8	298.16	1313.3
75	110.2	200	735.1	300	1324.4
100	211.7	225	879.1		

Jaffe and Campbell /26/ calculated the heat content with reference to zero degrees centigrade for solid zirconium from 100 to 600°.

T, °C	100	200	300	400	500	600
$H_T - H_{273}^0$, cal/g·atom	5.0	12.0	19.2	26.9	35.0	43.5

Kolsky and Gilles /21/ determined the heat content of gaseous zirconium.

T, °K	10	100	298.16	1000	3000	8000
$H_T - H_0^0$, cal/g·atom	49.6798	497.421	1629.07	6100.53	20056.5	65172.3

The heat content of solid zirconium was also determined by Kelley /22/:

T, °K	400	500	600	700	800	900
$H_T - H_{298}^0$, cal/g·atom	625	1270	1940	2650	3400	4180

The heat content according to Kelley /22/ is given by the following equation:

$$H_T - H_{298}^0 = 4.26 + 2.07 \cdot 10^{-3} T^2 - 0.56 \cdot 10^5 T^{-1} - 1266,$$

from 298 to 900°K. The accuracy of this equation is within 3%.

The following heat content values were calculated from the above equation:

T, °K	500	700	900
$H_T - H_{298}^0$, cal/g·atom	1270	2655	4202

Entropy of zirconium. The standard entropy of zirconium, according to various authors, is quoted in Table 176.

TABLE 176

Standard entropy of zirconium according to various authors

Entropy S_{298}^0, cal/g·atom·deg	Year	Author
	Solid zirconium	
9.5 ± 0.6	1917	Lewis, Gibson /27/
9.18 ± 0.08 at 25°	1949	Boulger /8/
9.28 + 0.08	1950	Todd /20/
9.29	1951	Skinner, Johnston /93/
9.3 ± 0.1	1951	Kubaschewski, Evans /16/
	Gaseous zirconium	
43.33 ± 0.1	1932	Bacher, Goudsmit /28/
43.32 ± 0.01	1950	Kelley /29/

The most reliable data in this table are those of Todd /20/, as quoted by Kubaschewski and Evans.

Skinner and Johnston /93/ calculated the entropy from experimental data on the heat capacity from 14 to 300°K. Their results are given in Table 177.

TABLE 177

Entropy of solid zirconium according to Skinner and Johnston /93/

T, °K	S_T^0 cal/g·at. deg	T, °K	S_T^0 cal/g·at. deg	T, °K	S_T^0 cal/g·at.deg
14*	0.030	125	4.421	250	8.240
25	0.169	150	5.359	275	8.807
50	1.016	175	6.139	298.16	9.292
75	2.200	200	6.942	300	9.014
100	3.362	225	7.621		

* Extrapolation to temperatures below 14°K according to Debye's law gave an entropy of 0.03 cal/mole·deg.

Table 178 gives the entropy of zirconium from 400 to 1400°K /24/.

TABLE 178

Entropy of zirconium according to Coughlin and King /24/

T, °K	$S_T^0 - S_{298}^0$ cal/g·at·deg	T, °K	$S_T^0 - S_{298}^0$ cal/g·at·deg	T, °K	$S_T^0 - S_{298}^0$ cal/g·at·deg
400	1.91	900	7.78	1135 (β)	10.42
500	3.44	1000	8.60	1200	10.82
600	4.74	1100	9.36	1300	11.40
700	5.88	1135 (α)	9.61	1400	11.94
800	6.88				

The data of Kelley /22/ for the entropy of zirconium are given below:

T, °K	400	500	600	700	800	900
$S_T - S_{298}^\circ$, cal/g·at.deg	1.8	3.24	4.46	5.56	6.56	7.47

Kolsky and Gilles /21/ give the following data on the entropy of gaseous zirconium:

T, °K	10	100	298.16	1000	3000	8000
S_T, cal/g·at.deg	25.7764	37.2226	43.3170	51.09	58.584	67.2918

Free energy function. From their own experimental data on the heat capacity, Skinner and Johnston /93/ calculated the Φ' function from 14 to 300°K (Table 179).

The Φ' and Φ'' functions for solid and gaseous zirconium at various temperatures are given in Tables 179 to 183.

Table 182 gives the values of the Φ' function calculated from the data of Tables 175 and 179, according to the equation

$$\Phi' = \Phi'' - \frac{H_{298}^\circ - H_0^\circ}{T} = \Phi'' - \frac{1313.3}{T}.$$

TABLE 179

Φ' function for solid zirconium according to Skinner and Johnston /93/

T, °K	$-\frac{(Z_T^0 - H_0^0)}{T}$ cal/g·atom·deg	T, °K	$-\frac{(Z_T^0 - H_0^0)}{T}$ cal/g·atom·deg	T, °K	$-\frac{(Z_T^0 - H_0^0)}{T}$ cal/g·atom·deg
14	0.008	125	1.776	250	4.137
25	0.043	150	2.297	275	4.536
50	0.296	175	2.795	298.16	4.887
75	0.430	200	3.267	300	4.914
100	1.245	225	3.714		

TABLE 180

Φ'' Function for solid zirconium according to Coughlin and King /24/

T, °K	Φ'' cal/g·atom·deg	T, °K	Φ'' cal/g·atom·deg	T, °K	Φ'' cal/g·atom·deg
400	9.53	800	11.72	1135(α)	13.45
500	10.02	900	12.28	1135(β)	13.45
600	10.50	1000	12.78	1200	13.8
700	11.16	1100	13.28	1300	14.3

TABLE 181

Φ' Function in cal/g·atom·deg for solid and gaseous zirconium, according to Skinner, Edwards, and Johnston /18/

T, °K	Φ'		T, °K	Φ'		T, °K	Φ'	
	Zr(s)	Zr (g)		Zr(s)	Zr (g)		Zr(s)	Zr (g)
1949	17.69	49.100	2007	17.94	49.285	2049	18.12	49.418
1980	17.82	49.200	2029	18.03	49.356	2054	18.14	49.434

TABLE 182

Φ' Function for solid zirconium, cal/g·atom·deg

T, °K	Φ'	T, °K	Φ'	T, °K	Φ'
400	6.30	900	10.82	1135 (β)	12.30
500	7.40	1000	11.74	1200	12.71
600	8.39	1100	12.09	1300	13.29
700	9.29	1135 (α)	12.30	1400	13.54
800	10.08				

TABLE 183

Φ'' Function for solid and gaseous zirconium, cal/g·atom·deg

T, °K	Φ'' (s)	Φ'' (g)	T, °K	Φ'' (s)	Φ'' (g)
1949	17.02	48.265	2029	17.38	48.556
1980	17.16	48.376	2049	17.78	48.623
2007	17.39	48.470	2054	17.50	48.641

We also calculated the Φ'' function for solid and gaseous zirconium from the data of Tables 180 and 184.

TABLE 184

Thermodynamic properties of [gaseous] zirconium considered as an ideal monoatomic gas /21/

T, °K	$-\frac{(F_T^0 - H_0^0)}{T}$ cal/g·atom·deg	$H_T^0 - H_0^0$ cal/g·atom	S_T^0 cal/g·atom·deg	C_p cal/g·atom·deg
10	20.8085	49.6798	25.7764	4.96798
20	24.2521	99.3595	29.2200	4.96798
30	26.2664	149.039	31.2343	4.96798
40	27.6956	198.719	32.6635	4.96798
50	28.8042	248.399	33.7721	4.96803
60	29.7100	298.081	34.6779	4.96857
70	30.4758	347.777	35.4440	4.97108
80	31.1393	397.518	36.1082	4.97826
90	31.7246	447.368	36.6953	4.99336
100	32.2485	497.421	37.2226	5.01913
110	32.7228	547.792	37.7027	5.05709
120	33.1565	598.604	38.1448	5.10735
130	33.5562	649.976	38.5559	5.16884
140	33.9272	702.012	38.9415	5.23973
150	34.2738	754.795	39.3057	5.31780
160	34.5992	808.385	39.6515	5.40017
170	34.9061	862.820	39.9815	5.48651
180	35.1970	918.118	40.2975	5.57317
190	35.4735	974.281	40.6012	5.65923
200	35.7372	1031.29	40.8936	5.74348
225	36.3489	1177.39	41.5817	5.94072
250	36.9043	1328.12	42.2168	6.11311
275	37.4144	1482.82	42.8064	6.25794
298.16	37.8533	1629.07	43.3170	6.36770
300	37.8869	1640.79	43.3562	6.37545
325	38.3276	1801.38	43.8703	6.46725
350	38.7409	1963.96	44.3522	6.53557
375	39.1303	2127.98	44.8048	6.58289
400	39.4984	2292.95	45.2307	6.61183
425	39.8475	2458.44	45.6320	6.62497
450	40.1795	2624.09	46.0107	6.62482
475	40.4959	2789.59	46.3687	6.61373
500	40.7981	2954.70	46.7074	6.59391
550	41.3642	3283.03	47.3333	6.53574
600	41.8856	3608.05	47.8990	6.46364
650	42.3683	3929.33	48.4133	6.38770
700	42.8171	4246.87	48.8840	6.31519
750	43.2362	4560.99	49.3175	6.25103
800	43.6290	4872.17	49.7192	6.19831
850	43.9984	5181.04	50.0937	6.15871
900	44.3469	5488.27	50.4449	6.13283
950	44.6766	5794.55	50.7761	6.12047
1000	44.9895	6100.53	51.0900	6.12090
1050	45.2872	6406.83	51.3889	6.13303
1100	45.5711	6714.00	51.6747	6.15551
1150	45.8425	7022.53	51.948	6.18692
1200	46.1024	7332.82	52.2131	6.22578
1250	46.3520	7645.21	52.4681	6.27065
1300	46.5920	7959.96	52.7150	6.32018
1350	46.8233	8277.29	52.9545	6.37314
1400	47.0464	8597.32	52.1873	6.42840
1450	47.2621	8920.15	53.4138	6.48491
1500	47.4708	9245.82	53.6346	6.54210
1550	47.6732	9574.35	53.8501	6.59902
1600	47.8695	9905.71	54.0605	6.65520
1650	48.0602	10239.9	54.2661	6.71022
1700	48.2457	10576.7	54.4672	6.76375
1750	48.4263	10916.2	54.6641	6.81588
1800	48.6023	11258.2	54.8568	6.86556
1850	48.7739	11602.7	55.0455	6.91365

TABLE 184 (continued)

T, °K	$-\frac{(F_T^0 - H_0^0)}{T}$ cal/g·atom·deg	$H_T^0 - H_0^0$ cal/g·atom	S_T^0 cal/g·atom·deg	C_p cal/g·atom·deg
1900	48.9414	11949.6	55.2305	6.95984
2000	49.2649	12650.0	55.5898	7.04680
2100	49.5743	13358.7	55.9355	7.12727
2200	49.8711	14075.2	56.2689	7.20246
2300	50.1563	14799.1	56.5906	7.27340
2400	50.4309	15529.9	56.9016	7.34230
2500	50.6958	16267.5	57.2027	7.40944
2600	50.9517	17011.8	57.4946	7.47612
2700	51.1993	17762.7	57.6680	7.54313
2800	51.4392	18520.4	58.0536	7.61104
2900	51.6720	19258.0	58.3219	7.68022
3000	51.8980	20056.5	58.5834	7.75078
3200	52.3317	21621.2	59.0883	7.89654
3400	52.7435	23215.4	59.5715	8.04696
3600	53.1358	24840.1	60.0358	8.19981
3800	53.5108	26495.3	60.4832	8.35219
4000	53.8703	28180.8	60.9154	8.50155
4200	54.2158	29895.4	61.3337	8.64399
4400	54.5486	31637.8	61.7389	8.77843
4600	54.8698	33406.1	62.1319	8.90265
4800	55.1804	35198.1	62.5132	9.01536
5000	55.4811	37011.4	63.8834	9.11571
5200	55.7728	38843.5	63.2426	9.20329
5400	56.0559	40691.9	63.5914	9.27796
5600	56.3311	42553.8	63.9300	9.33991
5800	56.5989	44427.0	64.2586	9.38951
6000	56.8595	46308.9	64.5776	9.42729
6200	57.1135	48197.2	64.8872	9.45388
6400	57.3612	50089.7	65.1876	9.46999
6600	57.6028	51984.5	65.4792	9.47637
6800	57.8386	53879.4	65.7620	9.47377
7000	58.0690	55773.5	66.0365	9.46295
7200	58.2940	57664.4	66.3029	9.44467
7400	58.5140	59550.9	66.5613	9.41964
7600	58.7291	61431.8	66.8121	9.38856
7800	58.9395	63305.9	67.6555	9.35208
8000	59.1453	65172.3	67.2918	9.31083

Kolsky and Gilles /21/ calculated the free energy, heat content, entropy, and heat capacity of gaseous zirconium, considered as an ideal monoatomic gas. The method of calculation was taken from Jaque*.

Figure 5 shows that the heat capacity, C_p, of zirconium passes through a maximum at approximately 435°K and a minimum at about 975°K.

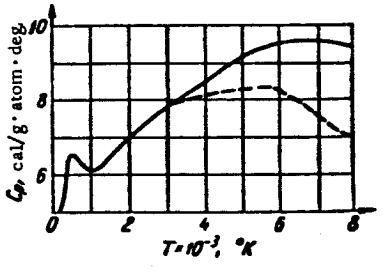

Figure 5. Atomic heat capacity of gaseous zirconium as a function of temperature (Kolsky and Gilles).

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* [Probably Jaffee.]

22. OXIDES OF ZIRCONIUM

Zirconium dioxide ZrO_2 (M = 123.21)

Allotropy of ZrO_2. Zirconium dioxide occurs in three crystallographic modifications: cubic /30/, tetragonal /31/, and monoclinic /32/.

The lattice parameters of solid solutions of oxygen in zirconium, as determined by Fast /33/, are presented in Table 185.

TABLE 185

Lattice parameters of solid Zr-O solutions

Oxygen content in at. %	Lattice parameters in Å	
	a	c
Pure	3.22	5.13
10	3.23	5.15
20	3.23	5.17
30	3.23	5.19

TABLE 186

Vapor pressure of ZrO_2 (Chupka, Berkowitz, and Inghram) /40/

Sample and container	T, °K	Vapor pressure, atm.
ZrO_2 in Ta	2421	$6.9 \cdot 10^{-8}$
ZrO_2 in Ta	2480	$5.9 \cdot 10^{-8}$
ZrO_2 in ThO_2	2331	$3.6 \cdot 10^{-8}$
ZrO_2 in crucible	2471	$1.4 \cdot 10^{-7}$
ZrO_2 (s) in ZrO	2374	$1.4 \cdot 10^{-7}$

Transition temperature of ZrO_2. When ZrO_2 is heated it undergoes a transition from the monoclinic form (i.e., distorted cubic-tetrahedral form with parameters a = 5.21, b = 5.26, c = 5.37 Å) into the tetragonal form. According to Dietul and Tober /34/ this occurs between 950 and 1150°. On the other hand, Kubaschewski and Evans /16/, and Brewer /35/ give this transition temperature as 1205°.

Oxygen absorbed by zirconium (amount not reported) increases the temperature of the $\alpha \rightarrow \beta$ transition to 1150° /30/.

According to De Boer and Fast /36/, oxygen absorbed by zirconium in an amount of 10 at. % increases the $\alpha \rightarrow \beta$ transition temperature to 1800°K.

Melting point of ZrO_2. Kelley /37/ gives the melting point of ZrO_2 as 2988°K. Kubaschewski and Evans /16/ report that the melting point of this compound is not lower than 2700°C. Brewer /35/ gives the melting point as 2960 ± 25°K.

Boiling point of ZrO_2. Mott /38/ determined the boiling point of ZrO_2 as 4570°K; Kubaschewski and Evans /16/ give an approximate value of 4300°C.

Vapor pressure of ZrO_2. Searcy /39/ calculated the vapor pressure at 2073°K and obtained the result $1.5 \cdot 10^{-7}$ atm.

Brewer /35/ reports that the vapor pressure of ZrO_2 is 10^{-6} atm at 2000°K.

Chupka, Berkowitz, and Inghram /40/, using mass spectrometric methods, determined the vapor pressure of solid ZrO_2 and of a mixture of Zr and ZrO_2 powders. Their results /40/ are summarized in Table 186.

Heat capacity of ZrO_2. Data on the heat capacity of solid ZrO_2 at low temperatures as given by Kelley /29/ are presented below:

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity, cal/mole·deg	0.02*	0.18*	1.21	4.55	7.77	10.32	13.42

The heat capacity of ZrO_2 from 273 to 1673°K is given by the following equation /29/:

$$C_p = 11.62 + 10.46 \cdot 10^{-3} T - 1.777 \cdot 10^5 T^{-2}.$$

The accuracy of this equation is 5%.

The values of the heat capacity of ZrO_2, calculated by this equation, are given below.

Temperature, °K	298	500	1000	1500
C_p, cal/mole·deg	12.7	15.14	21.903	27.3

In the range between 298 and 1100°K, the heat capacity of ZrO_2 is given by the following equation /22/:

$$C_p = 17.80 - 4.00 \cdot 10^5 T^{-2}.$$

Values of the heat capacity of ZrO_2, calculated from the above equation, are given below:

Temperature, °K	298	500	1000
C_p, cal/mole·deg	13.36	16.2	17.4

According to King and Coughlin /24/, the heat capacity of solid ZrO_2 obeys the following equation from 298 to 1478°:

$$C_p = 16.64 + 1.80 \cdot 10^{-3} T - 3.36 \cdot 10^5 T^{-2}.$$

Values of the heat capacity of ZrO_2, calculated from this equation, are given below:

Temperature, °K	298	500	1000	1400
C_p, cal/mole·deg	13.45	16.196	18.104	19.01

The heat capacity of solid β-zirconium is C_p = 17.80 cal/mole·degree between 1478 and 1850°K.

The accuracy of the first and second equation is 2%.

Heat of fusion of ZrO_2. Zhirnova /41/ studied the system ZrO_2 — SiO_2 and determined the heat of fusion of ZrO_2 as 20,100 cal/mole.

According to Ebert and Kohn /37/, who studied the system ZrO_2 — MgO, the heat of fusion of ZrO_2 is 21,000 cal/mole. Kelley /37/ considers an average value of these two results, i.e., 20,800 cal/mole to be the most reliable.

Heat of transition of ZrO_2. King and Coughlin /24/ give the heat of transition of ZrO_2 as L_{trans} = 1.42 ± 0.1 kcal/mole.

Entropy of fusion of ZrO_2. Kelley /37/ gives the entropy of fusion of ZrO_2 as ΔS_{fus} = 6.95 cal/mole·degree.

Entropy of transition of ZrO_2. King and Coughlin /24/ give the entropy of transition of ZrO_2 as 1.2 e.u.

Heat content of ZrO_2. The heat content of monoclinic ZrO_2 is given in Table 187 /42, 22/.

The heat content of ZrO_2 (Table 187) obeys the following equation from 298 to 1100°K:

$$H_T - H^*_{298} = 17.80 T + 4.00 \cdot 10^5 T^{-1} - 6.649.$$

The accuracy of this equation is 3%.

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* Extrapolated.

TABLE 187

Heat content of ZrO_2 according to Kelley /42, 22/

T, °K	$H_T^0 - H_{298}^0$ cal/mole	T, °K	$H_T^0 - H_{298}^0$ cal/mole
[42]		[22]	
373.1	1325	400	1470
473.1	3020	500	3040
573.1	4640	600	4690
673.1	6340	700	6360
873.1	10080	800	8050
1073.1	14400	900	9780
1273.1	19200	1000	11540
1473.1	24510	1100	13350

The heat content of ZrO_2, calculated from the above equation for three different temperatures, is given below:

Temperature, °K	298	500	1000
$H_T - H_{298}^0$, cal/mole	24.3	3051	11551

Entropy of ZrO_2. Kelley /43/ gives the following values for the entropy of ZrO_2: $S_{50}^0 = 0.44$ (extrapolated), $S_{298}^0 - S_{50}^0 = 11.68$ (experimental), and $S_{298}^0 = 12.12 \pm 0.08$ cal/mole · degree (calculated).

Kubaschewski and Evans /16/ quote Kelley /44/ and give the entropy of ZrO_2 as $S_{298}^0 = 12.03 \pm 0.1$ cal/mole · degree.

The changes in entropy of solid ZrO_2, as calculated by Kelley /22/, are given below:

Temperature, °K	400	500	600	700	800	900	1000	1100
$S_T^0 - S_{298}^0$, cal/mole · deg.	4.23	7.73	10.74	13.31	15.56	17.60	19.46	21.18

Heat of formation of ZrO_2. Table 188 presents the heat of formation of ZrO_2 as obtained by various authors:

TABLE 188

Heat of formation of ZrO_2

Heat of formation $-\Delta H_{298}^0$, kcal/mole	Year	Author	Reference
264.6 ± 0.2	1931	Rose, Becker [Landolt-Börnstein]	/45/
258.5 ± 1.0	1954	Kubaschewski, Evans	/16/
261.5 ± 0.2	1936	De Boer, Fast	/36/
261.5	1954	Humphrey	/46/
258.8 or 258.1	1934	Neumann et al.	/47/
256.1	1930	Sieverts	/48/
259.0 ± 1.5	The average result of the three last determinations		

The last three determinations were carried out with iodide zirconium. Brewer /35/ gives the heat content as $\Delta H_{298}^0 = -261.8 \pm 0.2$ kcal/mole.

The heat and the free energy of formation of ZrO_2, according to Coughlin /91/, are presented in Table 189.

TABLE 189

Heat and free energy of formation of ZrO_2 (α, β)

T, °K	$-\Delta H_T^0$ kcal/mole	$-\Delta F_T^0$ kcal/mole	T, °K	$-\Delta H_T^0$ kcal/mole	$-\Delta F_T^0$ kcal/mole
298.16	261.500 (±200)	247.750	1200	260.750	207.150
			1300	260.500	202.700
400	261.400	245.050	1400	260.200	198.250
500	261.250	238.450	1478 (α)	260.000	194.250
600	261.100	233.900	1478 (β)	258.550	194.850 (α)
700	260.900	229.400	1500	258.500	194.850 (β)
800	260.700	224.950	1600	258.350	193.850
900	260.500	220.450	1700	258.200	189.550
1000	260.300	216.050	1800	258.000	185.300
1100	260.100	211.600	1900	257.850	181.000
1135 (α)	260.000	210.050	2000	257.700	176.700
1135 (β)	260.950	210.050			172.450

The data of Table 189 may be calculated from the following formula:

$$\Delta H_T = \Delta H_0 - aT - b10^{-3}T^2 + 2c10^5 T^{-1}, \qquad (1)$$

which leads to

$$\Delta F_T^\circ = \Delta H_0 + 2.303aT \log T + b \cdot 10^{-3}T^2 + c10^5 T^{-1} + IT. \qquad (2)$$

Table 190 contains values of the constants (Coughlin /91/) in equations (2) and (1) for the determination of the free energy and heat of formation of ZrO_2, respectively.

TABLE 190

Constants in equations (1) and (2) for calculation of ΔF_T^0 and ΔH_T^0/91/

Reaction	Temperature range	$-\Delta H_0$	2.303 a	b	c	I
$Zr(\alpha) + O_2(g) = ZrO_2(\alpha)$	298—1135° K	262.980	−6.10	+16	+1.045	+65
$Zr(\beta) + O_2(g) = ZrO_2(\alpha)$	1135—1478° K	264.190	−5.09	−40	+1.48	+63
$Zr(\beta) + O_2(g) = ZrO_2(\beta)$	1478—2000° K	262.290	−7.76	+50	−20	+69

The same author /91/ also gives a simplified linear equation for the free energy. Its use is justified, since at elevated temperature the free energy approaches a constant value. For this reason, the author /91/ believes that the equation

$$\Delta F_T^\circ = A + BT$$

gives an approximate value for ΔF_T°.

Table 191 contains constants A and B for calculation of the free energy of formation of zirconium oxide from the linear equation given above.

This simplified equation is, however, empirical and has the disadvantage that it cannot be used for calculation of the heat or entropy of formation at different temperatures.

TABLE 191

Constants in the linear equation for the free energy of formation of ZrO_2 /91/

Reaction	Temperature range	A	B
$Zr(\alpha) + O_2(g) = ZrO_2(\alpha)$	298—1135° K	−261.030	+45.01
$Zr(\beta) + O_2(g) = ZrO_2(\alpha)$	1135—1478° K	−260.430	+44.40
$Zr(\beta) + O_2(g) = ZrO_2(\beta)$	1478—2000° K	−258.170	+42.87

Entropy of formation of ZrO_2. Kelley /49/ gives the entropy of formation of ZrO_2 as $\Delta S^{\circ}_{298} = -41.8$ cal/mole · degree.

Brewer /35/ gives the entropy of formation of ZrO_2 as $\Delta S^{0}_{298} = -23.1$ cal/mole · degree, while Kubaschewski and Dench /50/ give $\Delta S^{0}_{298} = -45$ cal/mole · degree.

TABLE 192

Heat of sublimation of ZrO and ZrO_2 from the method of absolute pressure /40/

Sample and container	T, °K	P, atm.	ΔF^{0}_{T} kcal/mole	ΔS^{0}_{T} e.u.	L_{subl} kcal/mole
ZrO; Zr + ZrO_2 in Ta	2173	$6.6 \cdot 10^{-7}$	61.4	39.0	146.1
	2124	$2.33 \cdot 10^{-7}$	64.4	39.1	147.4
	2322	$1.86 \cdot 10^{-5}$	50.2	38.8	140.3
	2137	$7.45 \cdot 10^{-7}$	59.9	39.1	143.5
				average	144.3
ZrO_2; ZrO_2 in Ta	2421	$6.9 \cdot 10^{-8}$	79.3	37.9	171.1
ZrO_2 in Ta	2480	$5.9 \cdot 10^{-8}$	82.0	37.8	175.7
Zr + ZrO_2 in Ta	2416	$4.8 \cdot 10^{-8}$	80.9	37.9	172.5
ZrO_2 in ThO_2	2331	$3.6 \cdot 10^{-8}$	79.4	38.0	168.0
Zr + ZrO_2 in Ta	2340	$2.1 \cdot 10^{-7}$	71.5	38.0	160.4
ZrO_2 (crucible)	2471	$1.4 \cdot 10^{-7}$	77.5	37.8	170.9
ZrO_2 in ZrO_2 (crucible)	2374	$1.4 \cdot 10^{-7}$	74.4	37.9	164.4
				average	169.0

TABLE 193

Heat of sublimation of ZrO_2 from slope of the vapor pressure curve /40/

Surrounding medium	Temperature, °K	L_{subl}, kcal/mole
ZrO_2; ZrO_2 in ThO_2	2245 — 2504	169.5
ZrO_2 (crucible)	2250 — 2450	172.0
ZrO_2 (crucible)	2200 — 2430	169.5
ZrO_2 in ZrO_2 (crucible)	2200 — 2430	173.7

Free energy of formation of ZrO_2. The free energy of formation of ZrO_2, according to various authors, is:

$$\Delta F^\circ_{298} = -252.14 \text{ kcal/mole } /49/;$$

$$\Delta F^\circ_{298} = -248.0 \text{ kcal/mole } /35/;$$

$$\Delta F^\circ_{298} = -247.7 \pm 0.2 \text{ kcal/mole } /46/.$$

The free energy of formation from 298 to 2000°K, according to the reaction

$$Zr\,(s) + O_2\,(g) = ZrO_2\,(s),$$

is given by the following equation /51/:

$$\Delta F^\circ_T = -260{,}300 - 10.15\,T \log T + 77.1\,T.$$

The accuracy of this equation is ±10 kcal. The following values of ΔF°_T for ZrO_2 were obtained from this equation:

Temperature, °K	298	500	1000	2000
ΔF^0_T, kcal/mole	-245.6	-235.4	-213.65	-176.5

Sublimation of ZrO_2. Chupka, Berkowitz, and Inghram /40/, using mass-spectrometric methods, determined the heat of sublimation of ZrO_2. The cell used contained either solid ZrO_2 (s) or a mixture of Zr and ZrO_2 powders. The cell was made from tantalum and a thorium crucible was placed in it. Later, the authors used crucibles made from ZrO_2. The temperatures were measured by means of an optical pyrometer.

The data of Chupka et al. /40/ for calculation of some of the thermodynamic properties of ZrO and ZrO_2 are given in Table 192.

The results of their calculations are given in Table 193.

23. HALIDES OF ZIRCONIUM

Zirconium tetrafluoride ZrF_4 (M = 167.22)

Crystal structure. Chretien and Indran /52/ studied the crystal structure of ZrF_4. These authors found a very sharp separation of the lines at 405 ± 5° on the X-ray diagram of ZrF_4. This indicated the presence of two different crystal forms: α and β ZrF_4. α-ZrF_4 is converted to β-ZrF_4 at 405°.

Vapor pressure of ZrF_4. Sense and co-workers /53/ determined the vapor pressure of ZrF_4 from 688 to 826°.and found that it obeys the following equation:

$$\log P(\text{mm Hg}) = 15.2206 - \frac{12{,}146.2}{T}.$$

The pressure, P, calculated from the above equation, has the following values:

Temperature, °K	1000	1050	1100
P, mm Hg	11.86	44.76	151.4

According to Fischer /54/, the vapor pressure of ZrF_4 from 910 to 1178° is given by the following equation:

$$\log P(\text{mm Hg}) = -11{,}420 \cdot T^{-1} + 12.57.$$

The pressure, P, calculated from this equation, has the following values:

Temperature, °K	1200	1300	1400
P, mm Hg	$11.75 \cdot 10^2$	$58.88 \cdot 10^2$	$23.44 \cdot 10^3$

Later, Sense and co-workers /55/ determined the vapor pressure of ZrF_4 from 616 to 881° by the "transpiration" method (Table 194) and found it to obey the following equation:

$$\log P(\text{mm Hg}) = -13.3995 + \frac{12,376}{T}.$$

From the above equation, the following values of P were obtained:

Temperature, °K	1000	1050	1100
P, mm Hg	10.54	40.64	140.9

Boiling point of ZrF_4. The boiling point of this compound was found by extrapolation /55/ to be 902°.

Sublimation temperature of ZrF_4. Sense and co-workers /55/ determined the sublimation temperature of ZrF_4 by extrapolation and obtained the value 903°. Kubaschewski and Evans /16/ give the value 907°.

Heat of sublimation of ZrF_4. According to Kubaschewski and Evans /16/, the heat of sublimation of ZrF_4 is 52.3 kcal/mole at 907°. Sense et al. /53/ give 55.55 kcal/mole. In a later work /55/, the same authors corrected their value to 56.63 ± 0.04 kcal/mole at 903°.

TABLE 194

Vapor pressure of ZrF_4 /55/

T, °C	Vapor pressure, mm Hg		T, °C	Vapor pressure, mm Hg	
	measured	calculated		measured	calculated
616.6	0.310	0.310	856.9	284	281.0
651.9	1.053	1.051	872.0	389	392
652.3	1.064	1.065	872.6	392	397
676.4	2.29	2.33	873.6	413	405
713.3	7.24	7.15	873.9	401	408
757.1	24.4	24.4	876.1	404	428
798.0	70.0	70.2	880.8	470	473
838.3	186.6	184.1			

Zirconium tetrachloride $ZrCl_4$ (M = 233.048)

Crystal structure of $ZrCl_4$. Solid $ZrCl_4$ has an SnI_4 type crystal lattice with a lattice parameter of 10.32 Å /56/.

Structure of $ZrCl_4$. According to Lister and Sutton /57/, the distance between the atoms of zirconium and chlorine in $ZrCl_4$ is 2.33±0.05 Å and the angle between the individual bonds 109°28'.

Melting point of $ZrCl_4$. Palko et al. /60/ determined the melting point of $ZrCl_4$ as 437°. The same value is given by Kubaschewski and Evans /16/. Kelley /58/ considers 710°K the most reliable value.

Sublimation temperature of $ZrCl_4$. Kelley /58/ gives 604°K as the sublimation temperature of $ZrCl_4$. Kubaschewski and Evans /16/ consider 331° the best value.

Vapor pressure of $ZrCl_4$. The vapor pressure of solid $ZrCl_4$ is given below /58/:

Temperature, °K	426.5	459.5	498.5	546	567.5	585.5	604
Saturated vapor pressure, at.	0.0_31	0.0_21	0.01	0.1	0.25	0.5	1.0

The same author /58/ derived the following equation for the vapor pressure of $ZrCl_4$ from 298 to 604°K:

$$\log P(\text{mm Hg}) = -6600\,T^{-1} - 1.61\log T - 1.78\cdot 10^{-3}T + 19.35.$$

The following values of P were obtained from the above equation:

Temperature, °K	298	400	500	600
P, mm Hg	0.0_556	0.033	8.128	648.6

Palko et al. /60/ give the following equation, valid for both solid and liquid $ZrCl_4$, from 480 to 689°K.

$$\log P(\text{mm Hg}) = -5400T^{-1} + 11.766.$$

This equation was obtained by use of the method of least squares. The following values of the pressure P were obtained from this equation:

Temperature, °K	500	600	650
P, mm Hg	11.64	583.4	2924.0

Palko and co-workers /60/ derived the following equation, valid from 710 to 741°K:

$$\log P(\text{mm Hg}) = -3427T^{-1} + 9.088.$$

Values of P calculated from this equation are as follows:

Temperature, °K	710	730	740
P, mm Hg	$1.811\cdot 10^4$	$2.443\cdot 10^4$	$2.742\cdot 10^4$

Heat capacity of $ZrCl_4$. The heat capacity of solid $ZrCl_4$ at low temperatures is given below /29/:

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity, cal/mole·deg	1.00*	4.68*	10.70	18.59	23.23	25.89	28.65

According to Kelley /29/, the heat capacity of solid $ZrCl_4$ obeys the following equation from 50 to 500°K:

$$C_P = 25.2 + 16.3\cdot 10^{-3}T \text{ cal/mole}\cdot\text{degree}.$$

C_P, calculated from this equation, has the following values:

Temperature, °K	50	100	150	200
C_P, cal/mole·deg	26.46	26.83	27.64	28.46
Temperature, °K	300	400	500	
C_P, cal/mole·deg	30.08	31.7	33.35	

The specific heat equation from 298 to 550°K is as follows:

$$C_P = 32.85 - 3.82\cdot 10^5 T^{-2} \text{ cal/mole}\cdot\text{degree}.$$

---

* Extrapolated.

The heat capacities calculated from this equation are given below:

Temperature, °K	298	400	500	550
C_P, cal/mole·deg	28.53	30.47	31.32	31.57

The heat capacity of gaseous $ZrCl_4$ is 22 cal/mole · degree.

King and Coughlin /24/ derived the following equation for the heat capacity of $ZrCl_4$:

$$C_P = 31.92 - 2.91 \cdot 10^5 T^{-2} \quad (2\%,\ 298°K - \text{temperature of sublimation}).$$

The heat capacity calculated from this equation has the following values:

Temperature, °K	298	400	500	600
C_P, cal/mole·deg	28.50	30.10	30.755	31.11

Heat of fusion of $ZrCl_4$. Kubaschewski and Evans /16/ give L_{fus} = 5.7 kcal/mole for the heat of fusion of $ZrCl_4$.

Palko and co-workers /60/ calculated the heat of fusion, L_{fus}, of $ZrCl_4$ as 9.0 ± 0.9 kcal/mole from vapor pressure data (difference between the heats of sublimation and vaporization). The accuracy of this value is within 15%.

The heat capacity change during sublimation of $ZrCl_4$ is expressed by the following equation:

$$\Delta C_P = -3.2 - 16.3 \cdot 10^{-3} T \text{ cal/mole} \cdot \text{degree} \ /58/.$$

Heat of sublimation of $ZrCl_4$. Zirconium tetrachloride sublimes at 331° and its heat of sublimation is 25.3 ± 2.5 kcal/mole /16/ at this temperature.

Palko and co-workers /60/ determined the heat of sublimation of this compound as 24.7 ± 0.3 kcal/mole.

Kelley /58/ derived the following equation expressing the heat of sublimation of $ZrCl_4$ as a function of absolute temperature:

$$L_{subl} = 30{,}200 - 3.2T - 8.15 \cdot 10^{-3} T^2 \text{ cal/mole}.$$

The values for the heat of sublimation determined from this equation are L_{298} = 28,552 cal/mole and L_{604} = 25,294 cal/mole.

Entropy of sublimation of $ZrCl_4$. ΔS^0_{604} = 41.9 cal/mole·degree, according to /58/, and ΔS^0_{298} = 49.1 cal/mole·degree, according to /29/, where $\Delta S°$ is the entropy of sublimation of $ZrCl_4$.

Free energy of sublimation of $ZrCl_4$. Kelley /58/ gives the following equation for the free energy of sublimation of $ZrCl_4$:

$$\Delta F^\circ_T = 30{,}200 + 7.37 T \log T + 8.15 \cdot 10^{-3} T^2 - 75.39 T,$$

hence, ΔF^0_{298} = 13,886 cal/mole.

Heat content of $ZrCl_4$. The values for the heat content of solid $ZrCl_4$ are given below:

Temperature, °C	350	400	450	500	550
$H^0_T - H^0_{298}$, cal/mole	1550	3065	4585	6105	7625

These data conform to the following equation:

$$H^\circ_T - H^\circ_{298} = 32.85 T + 3.82 \cdot 10^5 T^{-1} - 11{,}706 \text{ cal/mole}.$$

The accuracy of this equation is 2% from 350 to 550°K.

The heat content calculated from this equation has the following values:

Temperature, °K	400	500	550
$H_T^0 - H_{298}^0$, cal/mole	2399	5483	7089

Entropy of $ZrCl_4$. Kelley /29/ calculated the following entropy values from the heat capacity of $ZrCl_4$ from 52 to 297°K, according to Todd /61/: S_{51}^0 = 8.12 (extrapolated), $S_{298}^0 - S_{51}^0$ = 36.39 (experimental), and S_{298}^0 = 44.5± ?* cal/mole · degree (calculated).

Adding the last value to the value of the entropy of sublimation of solid $ZrCl_4$, ΔS_{298}^0 = 49.1, we obtain the entropy of gaseous $ZrCl_4$, S_{298}^0 = 93.6± 2 cal/mole · degree.

The entropy of solid $ZrCl_4$ at various temperatures is given below /22/:

Temperature, °K	350	400	450	500	550
$S_T^0 - S_{298}^0$, cal/mole · deg	480	884	1242	1562	1852

Heat of formation of $ZrCl_4$. Gross and co-workers /62/ determined experimentally the heat of formation of metallic zirconium and liquid chlorine at 25° and obtained the result −225.89 kcal/mole. The authors used this value to calculate the standard heat of formation and obtained the value −234.7 kcal/mole. It was found that the total error of the result did not exceed 0.4 kcal/mole.

Siemensen et al. /64/ determined the heat of formation of $ZrCl_4$ by direct chlorination of the metal in an enamelled calorimetric bomb. The authors obtained ΔH_{298}^0 = −231.9 ± 0.5 kcal/mole.

Bichowsky and Rossini /63/ give ΔH_{298}^0 = −230 kcal/mole for the heat of formation of $ZrCl_4$.

Zirconium tetrabromide $ZrBr_4$ (M = 410.884)

Melting point of $ZrBr_4$. According to Rahlfs and Fischer /59/, the melting point of $ZrBr_4$ is 727°K. Kubaschewski and Evans /16/ give 450°C.

Sublimation temperature of $ZrBr_4$. At normal pressure the sublimation temperature of $ZrBr_4$ is 630°K /58/. Kubaschewski and Evans /16/ give 357°C.

Vapor pressure of $ZrBr_4$. Rahlfs and Fischer /59/ studied the vapor pressure of solid zirconium tetrabromide. The authors showed that $ZrBr_4$ sublimes unchanged.

The vapor pressure of $ZrBr_4$ as determined by Rahlfs and Fischer /59/ is given below:

Temperature, °K	442.0	476.5	517.5	568	590.5	609.5	630
Vapor pressure, atm.	0.0_31	0.0_21	0.01	0.1	0.25	0.5	1.0

The vapor pressure of $ZrBr_4$ from 298°K to its sublimation temperature obeys the following equation /58/:

$$\log P(\text{mm Hg}) = -\frac{6780}{T} - 1.76 \log T - 1.65 \cdot 10^{-3} T + 19.60.$$

The above equation gives the following values of the vapor pressure:

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* [Data missing in original Russian manuscript.]

Temperature, °K	298	400	500	600
P, mm Hg	0.0_8837	0.0_2275	3.388	263

Heat capacity of $ZrBr_4$. Kelley /58/ gives the following equation for the heat capacity of solid $ZrBr_4$:

$$C_p = 25.5 + 15.1 \cdot 10^{-3} T \text{ (5\%, 298°K — temperature of sublimation)}$$

The following values for C_P were calculated from this equation:

Temperature, °K	298	400	500	600
C_p, cal/mole·deg	29.9	31.54	33.05	34.55

The heat capacity of gaseous $ZrBr_4$ is 22 cal/mole · degree.

Sublimation of $ZrBr_4$. The heat capacity change in this compound is given by the following equation /58/:

$$\Delta C_p = -3.5 - 15.1 \cdot 10^{-3} T.$$

Heat of sublimation of $ZrBr_4$. Kubaschewski and Evans /16/ give two values for the heat of sublimation of $ZrBr_4$:

$$L_{subl} = 25.8 \pm 2.5 \text{ kcal/mole at } 357°$$

and $$L_{subl} = 29.3 \pm 2.5 \text{ kcal/mole at } 25°.$$

The heat of sublimation is given by the following equation /58/:

$$L_{subl} = 31,000 - 3.5 \cdot T - 7.55 \cdot 10^{-3} T^2,$$

from which L_{298} = 29,286 cal/mole and L_{630} = 25,798 cal/mole.

Entropy of sublimation of $ZrBr_4$. The entropy of sublimation S^0_{670} of $ZrBr_4$ is 41.0 cal/mole · degree /58/.

Free energy of sublimation of $ZrBr_4$. Kelley /58/ gives the following equation for the free energy of sublimation of $ZrBr_4$:

$$\Delta F^\circ_T = 31,000 + 8.5 T \log T + 7.55 \cdot 10^{-3} T^2 - 76.53 T,$$

hence, ΔF°_{298} = 14,802 cal/mole.

Entropy of $ZrBr_4$. Kubaschewski and Evans /16/ give an approximate value only for the entropy of solid $ZrBr_4$, i.e., S^0_{298} = 61.0 cal/mole degree.

Heat of formation of $ZrBr_4$. The heat of formation of $ZrBr_4$, ΔH^0_{298}, is approximately −175.0 kcal/mole /65/.

Zirconium tetraiodide ZrI_4 (M = 598.86)

Melting point of ZrI_4. Kelley /58/, referring to the work of Rahlfs and Fischer /59/, gives the melting point of ZrI_4 as 772°K.

Sublimation temperature of ZrI_4. The sublimation temperature of ZrI_4 is 704°K /58/.

Vapor pressure of ZrI_4. The vapor pressure of solid zirconium tetraiodide was determined by Rahlfs and Fischer /59/. Their data are given below:

Temperature, °K	495	5.33	579	634	660.5	681.5	704
Pressure, atm.	0.0_31	0.0_21	0.01	0.1	0.25	0.5	1.0

The vapor pressure of solid ZrI_4 (s) from 298°K to the sublimation temperature is given by the following equation /58/:

$$\log P(\text{mm Hg}) = -7680 \cdot T^{-1} - 2.164 \log T - 1.344 \cdot 10^{-3} T + 20.87.$$

Heat capacity of ZrI_4. According to Kelley /58/, the heat capacity of solid ZrI_4 is given by the following equation:

$$C_p = 26.3 + 12.3 \cdot 10^{-3} T.$$

From this equation the following values were calculated for C_p at 300, 500, and 700°K:

Temperature, °K	300	500	700
C_p, cal/mole·deg	30.0	32.45	34.9

The heat capacity of gaseous ZrI_4 is 22 cal/mole · degree. The heat capacity change during sublimation of ZrI_4 is expressed by the equation /58/:

$$\Delta C_p = -4.3 - 12.3 \cdot 10^{-3} T \text{ cal/mole} \cdot \text{degree}.$$

Heat of sublimation of ZrI_4. The heat of sublimation of ZrI_4 is given by the following equation:

$$L_{subl} = 35{,}100 - 4.3T - 6.15 \cdot 10^{-3} T^2 \text{ cal/mole};$$

from which $L_{298} = 33{,}271$ and $L_{704} = 29{,}025$ cal/mole.

Kubaschewski and Evans /16/, referring to the data of Kelley /58/, give the following:

$$L_{subl} = 29.0 \pm 2.5 \text{ kcal/mole, at } 431°,$$

and $$L_{subl} = 33.3 \pm 2.5 \text{ kcal/mole, at } 25°.$$

Entropy of ZrI_4. Kubaschewski and Evans /16/ give as an approximation for the entropy of solid ZrI_4 $S^0_{298} = 67.5$ cal/mole · degree.

Heat of formation of ZrI_4. The heat of formation of ZrI_4, ΔH^0_{298}, is approximately 105.0 kcal/mole /16/.

24. ZIRCONIUM CARBIDE ZrC (M = 103.23)

Crystal structure of ZrC. The crystal structure of ZrC is an NaCl type cubic lattice with a lattice parameter of 4.67 Å /66/. According to other authors a = 4.685 kX /67/ or a = 4.669 Å /68/.

Density of ZrC. The density of ZrC calculated by Becker /69/ from X-ray analysis is 6.51 g/cm^3. Direct measurement of the density yielded /69/ 6.9 g/cm^3. Kieffer determined the density of ZrC /70/ as 6.7 g/cm^3.

Melting point of ZrC. According to Becker /69/, the melting point of ZrC is 3805 ± 125°K. Kubaschewski and Evans /16/ give 3500°K, Kieffer /70/ 3523°K.

Heat capacity of ZrC. By using the Debye equation, the following equation was determined for the heat capacity of zirconium carbide from 298 to 3000°:

$$C_p = 8.71 + 2.28 \cdot 10^{-3} T - 0.63 \cdot 10^5 T^{-2}.$$

This equation represents the experimental data quite well and may be used for calculation of the standard entropy from the formula $S^\circ_{298} = \int_0^{298} \frac{C_p}{T} dT$.

The entropy calculated in this manner is 8.05 cal/degree · mole and shows good agreement with the experimental value, 8.5 ± 1.5 cal/degree · mole.

Entropy of ZrC. Kubaschewski and Evans /16/ give S^0_{298} = 8.5 ± 1.5 cal/mole · degree for the entropy of ZrC. The entropy of ZrC calculated by Ulich /71/, according to Eastman's equation gave S^0_{298} = 5.0 ± 2 e.u.

Heat of formation of ZrC. The heat of formation, ΔH°_{298}, of ZrC according to the reaction Zr (s) + C (s) = ZrC (s) is −35,530 cal/mole /49/. Kubaschewski et al. /72/ give ΔH°_{298} = −40.0 ± 10.0 kcal/mole for the heat of formation of ZrC. Mah and Boyle /73/ determined the heat of formation of ZrC by combustion of the compound in a calorimetric bomb. They give ΔH_{298} * = −44.1 ± 1.5 kcal/mole. Prescott /84/ gives ΔH^0_{298} = −35.5 kcal/mole for the heat of formation of ZrC.

Entropy of formation of ZrC. Prescott /84/ gives S^0_{298} = 20.8 e.u. for the entropy of formation of ZrC. Kelley is of the opinion that this value for the entropy of formation of ZrC is high.

Free energy of formation of ZrC. Kelley /49/ gives for the free energy of formation of ZrC the following equation:

$$\Delta F^\circ_T = -35{,}530 - 20.7T,$$

from which ΔF°_{298} = −41,710 cal/mole. According to Kubaschewski and Evans /16/, the free energy of formation of ZrC, according to the reaction Zr (s) + C (s) = ZrC (s), may be calculated from the following equation:

$$\Delta F^\circ_T = -40{,}000 - 7.7\,T \text{ cal/mole } (\pm 15 \text{ kcal/mole, } 298 - 2000^\circ\text{K}).$$

Values of ΔF°_T at three different temperatures were calculated from this equation:

Temperature, °K	298	1000	2000
ΔF^0_T, kcal/mole	-42.25	-47.70	-55.40

25. NITRIDES OF ZIRCONIUM

Zirconium nitride ZrN (M = 105.928)

Crystal structure of ZrN. ZrN has a cubic lattice of the NaCl type. The lattice parameter according to /66/ is 4.63 Å. According to Duwez and Odell /67/, a = 4.567 kX. According to Becker /69/, a = 4.5745 ± 0.0001 Å at 17°.

Density of ZrN. The density of ZrN was calculated by Becker /69/ from X-ray data as 6.97 g/cm^3. By direct measurement Becker /69/ obtained the value 6.93 g/cm^3.

Coefficient of linear thermal expansion of ZrN. Becker /76/ studied the diffraction of powdered ZrN samples and obtained the following values for the coefficient of thermal expansion of ZrN (purity 99.95%): $6.0 \pm 0.5 \cdot 10^{-6}$ (from 17 to 455°) and $7.0 \pm 0.5 \cdot 10^{-6}$ degree^{-1} (from 17 to 680°).

Melting point of ZrN. According to Becker /69/, the melting point of ZrN is 3255 ± 50°K. Kubaschewski and Evans /69/ give 2950°.

Heat capacity of ZrN. The heat capacity of ZrN as determined by Kelley /19/ is given below:

* [Presumably ΔH°_{298}.]

Temperature, °K	10	25	50	100	150	200	298.16
Heat capacity, cal/mole·deg	0.01	0.15	1.04	3.72	5.91	7.60	9.66

The heat capacity of solid ZrN according to Naylor /75/ is given by the following equation:

$$C_p = 11.91 + 0.94 \cdot 10^{-3} T - 2.96 \cdot 10^{5} T^{-2} \text{ (1\%, 298—1800°*)}.$$

Values of the heat capacity of solid zirconium nitride were calculated from the above equation:

Temperature, °K	298	1000	1800
C_p, cal/mole·deg	8.892	12.554	13.504

Heat content of Zr_3N_2. According to Kelley /22/, the heat content of Zr_3N_2 is as follows:

Temperature, °K	400	500	600	700	800
$H_T^\circ - H_{298}^\circ$, cal/mole	3120	6460	10,060	13,970	18,020

These values conform to the equation:

$$H_T^\circ - H_{298}^\circ = 21.64\,T + 13.00 \cdot 10^{-3} T^2 - 7608 \text{ (5\%, 298 — 900°*)}.$$

Values of the heat content $H_T^\circ - H_{298}^\circ$ at three temperatures were calculated from this equation:

Temperature, °K	400	600	800
$H_T^\circ - H_{298}^\circ$, cal/mole	3122	10,072	17,442

Entropy of ZrN. The entropy of ZrN was calculated from the heat capacity data of Todd /61, 20/ and the following values obtained: $S_{51}^0 = 0.41$ (extrapolated), $S_{298}^0 - S_{51}^0 = 8.88$ (experimental), and $S_{298}^0 = 9.29 \pm 0.05$ cal/mole·degree (calculated). Kubaschewski and Evans /16/, quoting Todd /61/, give $S_{298}^\circ = 9.3 \pm 0.5$ cal/mole·degree.

Heat, entropy, and free energy of formation of ZrN. According to Hoch and co-workers /79/, $\Delta H_{298}^0 = -80.43$ kcal/mole for the heat of formation of ZrN. Kelley /49/, quoting Neumann /77/, gives $\Delta H_{298}^0 = -82,200$ cal/mole for the heat of formation of ZrN, according to the reaction $Zr\,(s) + \frac{1}{2} N_2 = ZrN\,(s)$. Neumann /77/ is also quoted by Kubaschewski and Evans /16/, who give $\Delta H_{298}^0 = -82.2 \pm 2.5$ kcal/mole.

Mah and Gellert /78/ calculated the following value: $\Delta H_{298}^\circ = -87 \pm 0.4$ kcal/mole.

Sublimation of ZrN. The sublimation of ZrN was carried out in a Knudsen cell at 1987 to 2241 and 2236° to 2966°K /81/. It was found that ZrN decomposes into solid Zr and gaseous N_2. The heat of decomposition was given by $\Delta H = 79.53$ kcal/mole.

The heat of formation of ZrN from solid Zr and gaseous nitrogen is therefore −79.53 kcal/mole /81/.

Entropy of formation of ZrN. Mah and Gellert /78/ report $\Delta S_{298}^0 = 22.9$ e.u. for the entropy of formation of ZrN. The same value is given by Kelley /29/.

Free energy of formation of ZrN. Kelley /49/ gives the following formula for the free energy of formation of ZrN:

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* [Obviously, °K are meant.]

$\Delta F_T^\circ = -82{,}200 + 22.0\,T$ cal/mole (±15 kcal/mole, 298—2000°K),

from which $\Delta F_{298}^0 = -75{,}640$ cal/mole.

Mah and Gellert /78/ calculated the free energy of formation of ZrN from calorimetric data and obtained $\Delta F_{298}^0 = -80.5$ kcal/mole.

In the region $ZrN_{1.0}O_{0.04}$ to $ZrN_{0.56}O_{0.02}$, Simagina and co-workers /80/ observed that the free energy varies from 81.1 to 52.3 kcal/mole.

26. REDUCTION OF ZIRCONIUM COMPOUNDS

Reduction of ZrO_2 by magnesium

The reduction of ZrO_2 by magnesium proceeds according to the following reaction: $ZrO_2 + 2Mg = Zr + 2MgO$.

Rutkowski /83/ reports that powdered zirconium (mixed with ZrH_2), containing 91 to 92% of Zr, was obtained by carrying out the reaction $ZrO_2 + 2Mg = Zr + 2MgO$, at 900 to 1500°, in a hydrogen atmosphere. The following approximate values for ΔF_T° were obtained for this reaction:

Temperature, °K	900	1000	1100	1200	1300	1400	1500
Free energy, kcal/mole	108.06	107.508	106.029	104.931	103.808	101.707	95.822

Reduction of ZrO_2 with carbon

The reduction of ZrO_2 with carbon proceeds according to the following reaction: $ZrO_2 + 3C = ZrC + 2CO$.

The equilibrium of this reaction was determined by Prescott /84/ from 1880 to 2015°K.

Lorenz and Woolcock /85/ studied the same reaction at 1743°K.

The vapor pressure carbon monoxide and $R \ln K$ value according to both /84/ and /85/ are given in Table 195.

TABLE 195

Vapor pressure of CO, atm.

T, °K	P_{CO}	$-R \ln K$
Values of Prescott /84/		
1880	0.522	2.58
1914	0.856	0.62
1948	1.210	-0.76
1982	1.670	-2.04
2015	2.320	-3.34
Values of Lorenz and Woolcock /85/		
1743	0.196	6.48

The authors /84, 85/ obtained the following equations for the reaction $ZrO_2 + 3C = ZrC + 2CO$:

$$\Delta H_T^\circ = 180{,}000 - 14T; \quad \Delta H_{298}^\circ = 175{,}830 \text{ cal/mole};$$

$$\Delta F_T^\circ = 180{,}000 + 32.2T\log T - 199.07T,$$

from which ΔF_{298}° = 144,410 cal/mole.

Kutsev and co-workers /86/ also studied the ZrO_2/C equilibrium at high temperatures. Reduction of ZrO_2 by carbon at 1800 to 2000°K and 150 to 1000 mm Hg did not produce ZrC, but an oxycarbide of the composition ZrC_xO_y according to the equation:

$$ZrO_2 + 2.63C = ZrC_{0.71}O_{0.08} + 1.92CO. \qquad (1)$$

Table 196 contains data on the equilibrium pressure and free energy of the above reaction (P = const). This table also contains data* on the lattice parameters of the oxycarbide formed. ΔF° was calculated from the exponential indexes of P_{CO}.

TABLE 196

Free energy $\Delta F^\circ = -RT\ln P^{1.92}$

T, °K	P, mm Hg	ΔF°, cal	T, °K	P, mm Hg	ΔF°, cal
1814	115	13100	1926	437	4020
1850	154	11230	1980	669	690
1900	302	6660	2020	935	1610

Using the method of Temkin and Shvartsman, the following data were obtained for the heat content, entropy, and free energy of reaction (1) from 1800 to 2000°K:

$$\Delta H^\circ = 138{,}000 \text{ cal},$$

$$\Delta S^\circ = 69.0 \text{ e.u. and } \Delta F = 138{,}000 - 69.0T.$$

The following standard values for the heat content, entropy, and free energy were obtained: ΔH^0_{298}, ΔS° and ΔF^0_{298}: ΔH^0_{298} = 154,000 cal; ΔS^0_{298} = 82.0 e.u., ΔF^0_{298} = 129,600 cal/mole.

The authors /86/ used the following data for calculation of the heat and entropy of formation of $ZrC_{0.71}O_{0.08}$:

for ZrO_2, ΔH^0_{298} = −258.8 kcal/mole /90/; S^0_{298} = 12.12 e.u. /22/;

for CO, ΔH^0_{298} = 26.6 kcal/mole /88/; S^0_{298} = 47.32 e.u. /87/;

for graphite, S^0_{298} = 1.36 e.u. /87/.

Calculation of the heat of formation and entropy of the oxycarbide $ZrC_{0.71}O_{0.08}$ yielded the following results: ΔH^0_{298} = −53.8 kcal/mole and S^0_{298} = 7.0 e.u.

Zirconium carbide reaction

Portnoi and Levinski** studied the equilibrium of reaction $ZrN + C \rightleftharpoons ZrC + \frac{1}{2}N_2$ (2) from 1800 to 2700°.

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* [These data were not in the table.]

** [No reference given in Russian text.]

The equilibrium was approached both from the oxidizing and reducing sides. Values of K_p determined by these authors are given in Table 197.

TABLE 197

Equilibrium constants of reaction (2) at various temperatures, according to Portnoi and Levinskii

starting compound	t, °C	K_p	starting compound	t, °C	K_p
ZrN	1700	—	ZrC	1700	1.78
	1810	1.85		1810	2.22
	1870	—		1870	2.33
	1930	2.07		1930	2.38
	2150	3.00		2150	3.08
	2370	4.88		2370	5.05
	2480	7.00		2480	6.70

The composition of the carbonitride formed was determined by X-ray analysis. The logarithm of the equilibrium constant was calculated by use of the following equation:

$$K_p = \sqrt{P_{N_2}}\,\frac{[ZrC]}{[ZrN]}.$$

Log K_p is given by the equation:

$$\log K_p = -\frac{5290}{T} + 2.76,$$

where T is the absolute temperature.

From the above equation the free energy of reaction (2) may be calculated:

$$\Delta F_T^\circ = 24.2 - 12.4T.$$

The equilibrium constant K_p of reaction (2) may also be given by another equation, which, however, does not take into account the variation of the heat capacity of the reacting substances with temperature:

$$\log K_p = -\frac{9200}{T} + 4.5.$$

The equilibrium constants K_p of reaction (2) calculated from this equation are given in Table 198.

TABLE 198

Variation of ΔF_T° and of the equilibrium constant of reaction (2) with temperature

T, °K	ΔF_T° cal/mole	$\log K_p$	K_p	T, °K	ΔF_T° cal/mole	$\log K_p$	K_p
290	36026	−26.431	$3.70\cdot10^{-27}$	2300	−5456	+0.518	3.29
1000	21480	− 4.695	$2.5\cdot10^{-5}$	2500	−9600	+0.839	6.90
1500	11120	− 1.620	$2.4\cdot10^{-2}$	2700	−13744	+1.112	12.94
1700	6976	− 0.897	0.13	2900	−17888	+1.349	22.34
1900	2823	− 0.325	0.47	3100	−22032	+1.553	35.73
2100	−1312	+ 0.136	1.36				

Chapter 5

THERMODYNAMIC PROPERTIES OF NIOBIUM AND OF ITS MORE IMPORTANT COMPOUNDS

27. METALLIC NIOBIUM (M = 92.91)

Crystal structure, melting point, vapor pressure

Crystal structure. Metallic niobium has a cubic body-centered lattice with the parameter a = 3.2941 ± 0.0003 kX at 20° /1/, or a = 3.3065 Å at 25° /2/.

Density of niobium. The density of niobium is 8.57 g/cm^3 at 20° /1, 3, 4/ (see also /5, 6, 7, 8, 9/).

Melting point of niobium. Reimann and Grant /10/ found that metallic niobium melts at 2770°K. Schofield /11/ determined the melting point of this metal as 2468°. Other authors give somewhat lower values /4, 7, 9, 12, 13/.

Vapor pressure of niobium. The vapor pressure of niobium was determined by Speiser, Blackburn, and Johnston, who used the Langmuir method /14/. The authors derived the following equation for the vapor pressure of niobium:

$$\log P\,(\text{atm}) = -\frac{40{,}169}{T} + 8.875.$$

The normal boiling point of niobium is approximately 3300° /3, 4/. Table 199 contains the experimental data of Speiser, Blackburn and Johnston /14/ and also the vapor pressure calculated from their equation.

TABLE 199

Vapor pressure of Niobium

Experimental		Calculated by equation (1)		Experimental		Calculated by equation (1)	
T, °K	P, atm	T, °K	P, atm	T, °K	P, atm	T, °K	P, atm
2304	$2.6311\cdot10^{-9}$	2000	$6.175\cdot10^{-12}$	2496	$5.7032\cdot10^{-8}$	2900	$1.056\cdot10^{-5}$
2325	$3.5216\cdot10^{-9}$	2100	$5.585\cdot10^{-11}$	2510	$6.418\cdot10^{-8}$	3000	$3.058\cdot10^{-5}$
2358	$8.0977\cdot10^{-9}$	2200	$4.134\cdot10^{-10}$	2528	$1.0132\cdot10^{-7}$	3100	$8.266\cdot10^{-5}$
2397	$1.2708\cdot10^{-8}$	2300	$2.572\cdot10^{-9}$	2545	$1.0657\cdot10^{-7}$	3200	$2.100\cdot10^{-4}$
2404	$1.6526\cdot10^{-8}$	2400	$1.374\cdot10^{-8}$	2555	$1.3963\cdot10^{-7}$	3300	$5.042\cdot10^{-4}$
2432	$2.2323\cdot10^{-8}$	2500	$6.418\cdot10^{-8}$	2566	$1.4626\cdot10^{-7}$	3400	$1.150\cdot10^{-3}$
2463	$4.0512\cdot10^{-8}$	2600	$2.663\cdot10^{-7}$	2580	$2.2127\cdot10^{-7}$	3500	$2.501\cdot10^{-3}$
2472	$4.1329\cdot10^{-8}$	2700	$9.945\cdot10^{-7}$	2596	$2.4438\cdot10^{-7}$	3600	$5.224\cdot10^{-3}$
2485	$5.8069\cdot10^{-8}$	2800	$3.381\cdot10^{-6}$				

Heat capacity of niobium. Brown, Zemansky, and Boorse /15/ determined the heat capacity of niobium at 2.5 to 11°K. The heat capacity of niobium in the temperature range between 64 and 76°K was determined by Cook, Zemansky, and Boorse /16/, but both papers give only a graphical presentation of the experimental data and no numerical values. Jaeger and Veenstra /8/ measured the heat capacity of niobium from 0 to 1600°, and their values are given in Table 200.

TABLE 200

Heat capacity of Niobium /8/

T, °C	Heat capacity		T, °C	Heat capacity	
	specific, cal/g · deg	atomic cal/g · atom · deg		specific, cal/g · deg	atomic cal/g · atom · deg
0	0.06430	6.012	900	0.07316	6.840
100	0.06510	6.087	1000	0.07437	6.954
200	0.06594	6.165	1100	0.07564	7.072
300	0.06683	6.249	1200	0.07695	7.195
400	0.06777	6.337	1300	0.07852	7.323
500	0.06875	6.428	1400	0.07973	7.455
600	0.06978	6.524	1500	0.08118	7.590
700	0.07086	6.626	1600	0.08267	7.731
800	0.07198	6.730			

According to Bolton /7/, the average specific and atomic heat capacities of niobium from 21 to 100° are as follows: C_p = 0.071 cal/g · degree and C_p = 6.67 cal/g · atom · degree.

Jaeger and Veenstra /8/ found that their atomic heat capacity data of niobium obey the following equation:

$$C_p = 6.0120 + 0.722533 \cdot 10^{-3} t + 0.21952 \cdot 10^{-6} t^2.$$

The atomic heat capacity as a function of absolute temperature is given by the following equation according to Kelley /17/:

$$C_P = 5.66 + 0.96 \cdot 10^{-3} T \ (1\%, \ 298 \text{ to } 1900°K).$$

According to this equation the following values for the heat capacity of niobium have been obtained:

$t°$, C	0	500	1000	1600
C_p, cal/g · atom · deg	5.922	6.402	6.882	7.458

Heat of fusion of niobium. Stull and Sinke /18/ give L_{fus} = 6400 cal/g · atom for the heat of fusion of niobium at 2770°K.

Heat of vaporization of niobium. Stull and Sinke /18/ calculated the heat of vaporization of niobium from the data of Reimann and Grant /10/ and obtained the following values: 177,500 cal/g · atom, and 166,500 cal/g · atom at 298 and 5200°K, respectively. Speiser, Blackburn, and Johnston /14/ calculated the heat of vaporization at 298°K from their experimental values as 172,530 cal/g · atom.

Heat content of niobium. The following equation for the heat content of solid niobium can be derived from Kelley's equation /17/ for the heat capacity:

$$H_T - H^0_{298} = 5.66\,T + 0.48 \cdot 10^{-3} T^2 - 1730 \text{ cal/g} \cdot \text{atom}.$$

Assuming $H^0_{298} - H^0_0 = 1264$ cal/g · atom /18/, the heat content values of solid niobium in Table 201 are obtained.

TABLE 201

Heat content, entropy, Φ' and Φ'' of solid niobium

T, °K	$H^\circ_T - H^\circ_T$ cal/g-at.	S°_T	Φ'	Φ''	T, °K	$H^\circ_T - H^\circ_T$ cal/g-at.	S°_T	Φ'	Φ''
		cal/g · atom · deg					cal/g · atom · deg		
298	1264	8.73	4.49	8.73	1500	9100	19.03	12.96	13.81
300	1275	8.77	4.52	8.74	1600	9810	19.49	13.36	14.15
400	1870	10.49	5.81	8.97	1700	10540	19.93	13.73	14.48
500	2480	11.85	6.89	9.41	1800	11270	20.35	14.09	14.79
600	3100	12.98	7.81	9.92	1900	12020	20.75	14.42	15.09
700	3730	13.94	8.61	10.42	2000	12770	21.13	14.74	15.38
800	4370	14.80	9.34	10.92	2100	13530	21.51	15.07	15.67
900	5010	15.56	9.99	11.40	2200	14310	21.87	15.37	15.94
1000	5670	16.25	10.58	11.84	2300	15090	22.21	15.65	16.20
1100	6340	16.89	11.13	12.28	2400	15880	22.55	15.93	16.46
1200	7010	17.48	11.64	12.69	2500	16680	22.88	16.21	16.72
1300	7700	18.02	12.10	13.07	2600	17490	23.20	16.47	16.96
1400	8390	18.54	12.55	13.45	2700	18310	23.51	16.73	17.20

Entropy of niobium. Stull and Sinke /18/ calculated the entropy of solid niobium from the data of Brown, Zemansky, and Boorse /15/, and obtained $S^0_{298} = 8.73$ cal/at · degree. If we use this value together with Kelley's equation for the heat capacity /17/, we obtain for solid niobium the formula:

$$S^\circ_T = -23.81 + 13.035 \log T + 0.96 \cdot 10^{-3} T.$$

Values for the entropy calculated from this equation are also given in Table 201.

Table 201 also contains values of the functions Φ' and Φ'', calculated from the following equations:

$$\Phi' = -\frac{F^\circ_T - H^\circ_0}{T} = -\frac{H^\circ_T - H^\circ_0}{T} + S^\circ_T,$$

$$\Phi'' = -\frac{F_T - H^\circ_{298}}{T} = -\frac{H^\circ_T - H^\circ_{298}}{T} + S^\circ_T.$$

28. OXIDES OF NIOBIUM

Niobium pentoxide Nb_2O_5 ($M = 265.82$)

Crystal structure of Nb_2O_5. Niobium pentoxide exists at least in two different allotropic modifications. Brauer /80/ found low-temperature, medium-temperature, and high-temperature modifications with the

respective points of transition at 850° and above 1100°. Holtzberg et al. /81/ found two crystal modifications, i.e., γ-Nb_2O_5 (435 to 830°) and α-Nb_2O_5 (above 830°). There are indications that other modifications of Nb_2O_5 exist /82—85/. In the following pages we shall only discuss the high-temperature modification of Nb_2O_5, unless otherwise stated.

Density of Nb_2O_5. According to various authors, the density of Nb_2O_5 is in the range 4.36 to 5.17 g/cm^3 /81, 86—89/. Holtzberg et al. /81/ found that for amorphous Nb_2O_5 d_{25} = 4.36 g/cm^3, for γ-Nb_2O_5 d_{25} = 5.17 g/cm^3, and for α-Nb_2O_5 d_{25} = 4.55 g/cm^3.

Melting point of Nb_2O_5. Table 202 contains data of various authors on the melting point of Nb_2O_5.

TABLE 202

Melting point of Nb_2O_5

Melting point	Year	Author	Reference
1733	1941	Brauer	/80/
1785	1953	Orr	/90/
1759	1955	Reisman, Holtzberg	/91/
1764	1957	Holtzberg et al.	/81/
1780	1960	Gel'd, Kusenko	/92/

Heat capacity of Nb_2O_5. The true heat capacities of Nb_2O_5 at low temperatures were determined by King /93/. His data are shown in Table 203.

TABLE 203

Heat capacity of Nb_2O_5

T, °K	C_P cal/mole·deg	T, °K	C_P cal/mole·deg	T, °K	C_P cal/mole·deg
53.24	5.127	114.54	15.39	216.60	26.54
57.12	5.716	124.62	16.85	228.17	27.40
61.25	6.426	136.03	18.42	236.41	27.98
65.58	7.206	146.32	19.76	245.82	28.57
70.06	7.977	155.98	20.89	256.19	29.20
74.52	8.732	166.28	22.04	266.49	29.81
80.17	9.721	176.36	23.06	276.76	30.44
84.45	10.48	186.11	24.02	286.50	30.98
94.75	12.21	196.13	24.88	296.64	31.45
104.36	13.76	206.15	25.69	298.16	31.57

Orr /90/, and Gel'd and Kusenko /92/ determined the heat contents of Nb_2O_5 in a wide range of temperatures and proposed equations for variation of the heat capacity of Nb_2O_5 with temperature. Orr /90/ derived the following equations: $C_P = 36.23 + 5.54 \cdot 10^{-3} T - 4.88 \cdot 10^5 T^{-2}$ (0.5%, 298 to 1785°K), C_P = 57.90 (0.1%, 1785 to 1810°K).

According to Gel'd and Kusenko /92/, the equation for the variation of heat capacity with temperature is given by: $C_P = 38.76 + 3.54 \cdot 10^{-3} T - 7.318 \cdot 10^5 T^{-2}$ (0.1%, 298 to 1780°K).

Table 204 presents heat capacities calculated from these equations.

Gel'd's and Kusenko's equation /92/ is to be preferred since their value for $C_{P_{298}}$ is in better agreement with that of 31.57 cal/mole·degree determined by

King /93/. Equations for the variation of heat capacity with temperature proposed by Kelley /67/ and reported by Kubaschewski and Evans /31/, and Britske et al. /94/ in their reference books are based on old values obtained by Krüss and Nilsen /95/, and are less reliable.

TABLE 204

True heat capacity of Nb_2O_5 in cal/mole · deg.

T, °K	C_p [90]	C_p [92]	T, °K	C_p [90]	C_p [92]	T, °K	C_p [90]	C_p [92]
298	32.39	31.58	800	39.90	40.45	1400	43.74	43.35
400	35.40	35.61	1000	41.28	41.57	1600	44.90	44.13
600	38.19	38.85	1200	42.54	42.50	1780	45.94	44.83

Heat of fusion of Nb_2O_5. Orr /90/ found L_{fus} = 24,590 cal/mole at 1785°K, Gel'd and Kusenko /92/ found L_{fus} = 24,770 cal/mole at 1780°K. We consider that the average value of the heat of fusion, 24,680 cal/mole at 1780°K, is the best for metallurgical calculations.

Heat content of Nb_2O_5. Table 205 contains the experimental data of Orr /90/ and Gel'd and Kusenko /92/ on the heat content of Nb_2O_5.

TABLE 205

Heat content of Nb_2O_5, cal/mole

T, °K	$H_T - H^0_{298}$	Reference	T, °K	$H_T - H^0_{298}$	Reference
381.4	2720	/90/	1396.6	43720	/90/
390.4	3040	/90/	1409	44521	/92/
384.1	6370	/90/	1491.3	47810	/90/
461	5508	/92/	1503	48216	/92/
582.2	10050	/90/	1535	49772	/92/
644	12841	/92/	1589.4	52190	/90/
686.7	14130	/90/	1638	54575	/92/
734	16333	/92/	1653.7	55110	/90/
791.2	18250	/90/	1706.4	57500	/90/
819	19468	/92/	1731.8	58910	/90/
890.8	22320	/90/	1742	59860	/92/
917	23714	/92/	1750.6	60360	/90/
1004.5	27060	/90/	1768	62423	/92/
1048	29065	/92/	1769.1	71000	/90/
1097.4	30960	/90/	1779.9	81170	/90/
1098	31231	/92/	1781	66732	/92/
1199	35370	/92/	1792.8	86130	/90/
1199,7	35290	/90/	1795	86313	/92/
1295.4	39280	/90/	1809.2	87080	/90/
1306.1	39800	/90/	1815	86668	/92/
1314	40329	/92/	1828	87887	/92/

Orr /90/ gives the following equations for the variation of the heat content of Nb_2O_5 with temperature:

$$H_T - H^\circ_{298} = 36.23\,T + 2.77 \cdot 10^{-3} T^2 + 4.88 \cdot 10^5 T^{-1} - 12{,}685 \quad (0.5\%,\ 298 \text{ to } 1785°K);$$

$$H_T - H^\circ_{298} = 57.90\,T - 17{,}673 \quad (0.1\%,\ 1785 \text{ to } 1810^\circ\text{K}).$$

The equation of Gel'd and Kusenko /92/, valid from 298 to 1740°K, is as follows:

$$H_T - H^\circ_{298} = 38.76\,T + 1.77 \cdot 10^{-3} T^2 + 7.318 \cdot 10^5 T^{-1} - 14{,}162.$$

Entropy of Nb_2O_5. King /93/ calculated the entropy, $S^0_{298} = 32.8 \pm 0.2$ cal/mole · degree, from the heat capacity data of Nb_2O_5 at low temperatures. Extrapolation from 51 to 0°K gives 2.51 cal/mole · degree.

If we use Gel'd's and Kusenko's /92/ equation for C_P we obtain the following equation for the variation of entropy of Nb_2O_5 with temperature:

$$S^\circ_T = -193.22 + 89.26 \log T + 3.54 \cdot 10^{-3} T + 3.659 \cdot 10^5 T^{-2}.$$

Values of the entropy, S°_T, calculated from this equation, are given below:

Temperature, °K	298	400	600	800
S°_T, cal/mole · deg	32.8	42.78	57.90	69.32

Temperature, °K	1000	1200	1400	1600	1780
S°_T, cal/mole · deg	78.47	86.13	92.74	98.58	103.32

Combining the equations for $H_T - H^0_{298}$ and S°_T, we obtain an equation for the free energy function, Φ'', as a function of temperature:

$$\Phi'' = -\frac{F^\circ_T - H^\circ_{298}}{T} = -\frac{H^\circ_T - H^\circ_{298}}{T} + S^\circ_T,$$

$$\Phi'' = -231.98 + 89.26 \log T + 1.77 \cdot 10^{-3} T - 3.659 \cdot 10^5 T^{-2} + \frac{14{,}162}{T}.$$

The values of the Φ'' function calculated from this equation are as follows:

Temperature, °K	298	400	600	800	1000
Φ'', cal/mole · deg	32.8	34.11	39.64	45.73	51.36

Temperature, °K	1200	1400	1600	1780
Φ'', cal/mole · deg	56.55	61.27	65.56	69.15

Heat of formation of Nb_2O_5. Table 206 contains results for the heat of formation of Nb_2O_5 as determined by combustion:

TABLE 206

Heat of formation of Nb_2O_5

$-\Delta H^0_{298}$, kcal/mole	Year	Author	Reference
463.1	1933	Becker, Roth	/96/
455.2	1954	Humphrey	/97/
472.6	1959	Morozova, Getskina	/98/
458.6	1960	Kusenko, Gel'd	/59/

The great discrepancies in ΔH^0_{298} are due to the fact that metallic niobium in varying degrees of purity was used.

We consider that Humphrey's /97/ result, $\Delta H^0_{298} = -455.2$ kcal/mole, based on work using niobium of the highest purity, is the most reliable. If we use Kelley's equation (p. 164) for the heat capacity of niobium, the equation derived by Gel'd and Kusenko (p. 166) for the heat capacity of Nb_2O_5 and the following equation for the heat capacity of O_2:

$$C_p = 8.27 + 0.26 \cdot 10^{-3} T - 1.88 \cdot 10^5 T^{-2} \text{ (3\%, 80 to 1700°)},$$

we obtain the following equation for the heat of formation of Nb_2O_5 according to the reaction $2Nb + \frac{5}{2} O_2 = Nb_2O_5$:

$$\Delta H^\circ_T = -458{,}140 + 6.765 T + 0.485 \cdot 10^{-3} T^2 + 2.618 \cdot 10^5 T^{-1}.$$

The heats of formation calculated from this equation are as follows:

t, °C	25	500	1000	1500
ΔH°_t, cal/mole	-455200	-452280	-448540	-444480

Entropy of formation of Nb_2O_5. The entropy of formation of this compound according to the reaction $2Nb + \frac{5}{2} O_2 = Nb_2O_5$ may be calculated as $\Delta S^0_{298} = -107.21$ cal/mole · degree from data given in the present work.

From the equations for ΔH°_T (p. 168) and ΔF°_T, the following equation for the variation in the entropy of formation of niobium pentoxide with temperature is obtained:

$$\Delta S^\circ_T = -147.53 + 15.58 \log T + 0.97 \cdot 10^{-3} T + 1.309 \cdot 10^5 T^{-2},$$

from which $\Delta S^0_{298} = -107.22$ cal/mole · degree.

The free energy of formation of Nb_2O_5 calculated from the data presented above and the third law [of thermodynamics] is given by $\Delta F^\circ_{298} = -423{,}250$ cal/mole.

Using $\Delta H^0_{298} = -455{,}200$ cal/mole and the heat capacities of niobium (p. 164), Nb_2O_5 (p. 166), and O_2 (see above equation), we obtain the equation:

$$\Delta F^\circ_T = -458{,}140 - 15.58 \cdot T \log T - 0.485 \cdot 10^{-3} T^2 + 1.309 \cdot 10^5 T^{-2} + 154.30 T.$$

Values of the free energy of formation of Nb_2O_5 calculated from this equation are as follows:

t, °C	25	500	1000	1500
ΔF°_T, cal/mole	-423250	-373770	-323980	-1275760

Niobium dioxide NbO_2 (M = 124.91)

Crystal structure of NbO_2. Niobium dioxide has a tetragonal lattice, close to the rutile type /80, 99—103/, with the following lattice parameters: a = 4.82 kX, b = 2.99 kX /103/, and a = 4.77 kX, b = 2.98 kX /100/.

The density of NbO_2 is 5.98 g/cm^3 /101/.

Heat capacity of NbO_2. The heat capacities of this compound at low temperatures were determined by King /104/. His results are presented in Table 207.

TABLE 207

Heat capacity of NbO_2

T, °K	C_p cal/mole · deg	T, °K	C_p cal/mole · deg	T, °K	C_p cal/mole · deg
53.45	1.733	114.69	6.066	216.49	11.37
58.11	2.026	124.96	6.763	226.25	11.75
62.58	2.341	136.02	7.452	236.23	12.05
67.17	2.667	145.71	8.054	245.71	12.37
71.77	3.004	156.03	8.635	256.53	12.70
76.56	3.342	165.95	9.156	266.33	12.97
81.56	3.718	176.26	9.662	276.19	13.23
86.26	4.058	185.96	10.14	286.82	13.47
95.12	4.700	196.07	10.57	296.30	13.74
104.85	5.396	206.31	10.99	298.15	(13.74)

Gel'd and Kusenko /92/ determined the heat content of NbO_2 and obtained the following equations for variation of heat capacity with temperature:

$$C_p = 14.681 + 6.156 \cdot 10^{-3} T - 2.421 \cdot 10^5 T^{-2} \text{ (1\%, 298 to 1040°K);}$$

$$C_p = 21.28 \text{ cal/mole} \cdot \text{degree (1\%, 1040 to 1700°K).}$$

The values for the heat capacities of NbO_2 calculated from this equation are quoted below:

Temperature, °K	298	400	600	800	
C_p, cal/mole · deg	13.79	15.63	17.70	19.23	
Temperature, °K	1000	1200	1400	1600	1800
C_p, cal/mole · deg	20.60	21.28	21.28	21.28	21.28

Heat of transition of NbO_2. The heat of transition of NbO_2 at 1040°K is 700 cal/mole.

Melting point of NbO_2. No data available.

Heat content of NbO_2. The heat content of NbO_2, calculated by Gel'd and Kusenko /92/, is presented in Table 208.

TABLE 208

Heat content of NbO_2 according to Gel'd and Kusenko /92/

T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole
457	2414	1042	13692	1198	17526
523	3560	1054	13928	1318	20072
646	5637	1065	14248	1407	21808
739	7327	1072	14573	1501	23762
843	9328	1084	14887	1514	24051
913	10701	1118	15829	1717	28437
1005	12750				

The authors /92/ found that their data conform to the following equations: from 298 to 1040°K:

$$H_T - H^\circ_{298} = 14.681\,T + 3.078 \cdot 10^{-3} T^2 + 2.421 \cdot 10^5 T^{-1} - 5460;$$

and from 1040 to 1700°K:

$$H_T - H^\circ_{298} = -8060 + 21.28T.$$

Entropy of NbO_2. King /104/ calculated the entropy of this compound from data on the heat capacities of NbO_2 at low temperatures and gave $S^\circ_{298} = 13.03 \pm 0.07$ cal/mole · degree.

Extrapolation from 51°K to 0°K yields the value 0.62 cal/mole · degree.

Using the equation of Gel'd and Kusenko (p. 166) for C_p, we obtain the following equation for the variation of the entropy of NbO_2 with temperature: from 298 to 1040°K:

$$S^\circ_T = -73.84 + 33.81 \log T + 6.156 \cdot 10^{-3} T + 1.21 \cdot 10^5 T^{-2};$$

from 1040 to 1700°K:

$$S^\circ_T = -112.52 + 49.01 \log T.$$

The entropy values calculated from these equations are given in Table 209.

TABLE 209

Entropy of NbO_2, cal/mole · deg

T, °K	S^0_T	T, °K	S^0_T	T, °K	S^0_T
298	13.03	1000	33.87	1400	41.67
400	17.36	1040	34.67	1600	44.51
600	24.12	1040	35.34	1800	47.02
800	29.42	1200	38.39		

Combining the equations for $H_T - H^0_{298}$ and S°_T, we obtain an equation for the free energy function as a function of temperature:
from 298 to 1040°K:

$$\Phi'' = -\frac{F^\circ_T - H^\circ_{298}}{T} = -\frac{H_T - H_{298}}{T} + S^\circ_T,$$

$$\Phi'' = -88.52 + 33.81 \log T + 3.078 \cdot 10^{-3} - 1.21 \cdot 10^5 \cdot T^{-2} + 5460/T;$$

and from 1040 to 1700°K:

$$\Phi'' = -133.80 + 49.01 \log T + 8060/T.$$

Values for the Φ'' function calculated from these equations are given in Table 210.

TABLE 210

Φ'' Functions for NbO_2

T, °K	Φ''	T, °K	Φ''	T, °K	Φ''
298	13.03	1000	21.33	1400	26.15
400	14.58	1040	21.82	1600	28.27
600	16.02	1200	23.83	1800	30.22
800	18.72				

Heat of formation of NbO_2. Table 211 contains values for the heat of formation of NbO_2 as proposed by various authors.

TABLE 211

Heat of formation of NbO_2

$-\Delta H^0_{298}$ cal/mole	Author	Year	Reference
190900	Mah	1958	/105/
189500	Kubaschewski, Evans	1958	/31/
199300	Morozova, Getskina	1959	/98/
191700	Kusenko, Gel'd	1960	/59/

Mah /105/, Morozova and Getskina /98/, and Kusenko and Gel'd /59/ ignited NbO_2 in a calorimetric bomb and obtained for the reaction $2NbO_2 + {}^1/_2O_2 = Nb_2O_5$:

$$\Delta H^\circ_{298} = -36{,}670 \text{ cal /105/},$$

$$\Delta H^\circ_{298} = -37{,}000 \text{ cal /98/, and}$$

$$\Delta H^\circ_{298} = -37{,}610 \text{ cal /59/}.$$

If we use the mean value $\Delta H^0_{298} = -37{,}100$ cal [for the above reaction] and $\Delta H^0_{298} = 455{,}200$ cal/mole for the heat of formation of Nb_2O_5 (p. 169), we obtain for the reaction $Nb + O_2 = NbO_2$, $\Delta H^0_{298} = -190{,}500$ cal. The authors of this book recommend the use of this value for thermodynamic calculations.

Using the equations given in this book for the heat capacities of Nb, NbO_2, and O_2, and the results $\Delta H^\circ = -190{,}500$ and $L_{1040} = 700$ cal/mole for NbO_2, we obtain the following equations for the heat of formation:

for solid NbO_2 (298 to 1040°K):

$$\Delta H_T = -191{,}125 + 0.751\,T + 2.468 \cdot 10^{-3} T^2 + 0.541 \cdot 10^5 T^{-1},$$

and for liquid NbO_2 (1040 to 1700°K):

$$\Delta H_T = -193{,}725 + 7.35\,T - 0.61 \cdot 10^{-3} T^2 - 1.88 \cdot 10^5 T^{-1}.$$

The following values for ΔH_T were obtained from this equation:

t, °C	25	500	1000	1500
ΔH_T, cal/mole	190500	189000	185500	182700

Entropy of formation of NbO_2. If the values for S^0_{298} given in this reference book are used, the following entropy of formation is obtained for the reaction $Nb + O_2 = NbO_2$:

$$\Delta S^\circ_{298} = -44.72 \text{ cal/mole} \cdot \text{degree}.$$

From the equations for ΔH_T and ΔF°_T (p. 173) we obtain:
from 298 to 1040°K:

$$\Delta S^\circ_T = -50.79 + 1.73 \log T + 4.936 \cdot 10^{-3} T + 0.27 \cdot 10^5 T^{-2};$$

and from 1040 to 1700°K:

$$\Delta S^\circ_T = -89.46 + 16.93 \log T - 1.22 \cdot 10^{-3} T - 0.94 \cdot 10^5 T^{-2}.$$

Free energy of formation of NbO_2*. If the values of this reference book are used, the free energy of formation of NbO_2 according to the third law of thermodynamics is given by $\Delta F^0_{298} = 177{,}170$ cal/mole.

* [In Russian text: Nb_2O_5.]

Using this value for the free energy of formation, $\Delta H^0_{298} = -190{,}500$ cal/mole, the heat capacities of NbO_2 (p. 170) and of O_2 (p. 169), the following equations are obtained:
from 298 to 1040°K:

$$\Delta F^\circ_T = -191{,}125 - 1.73\,T\log T - 2.468\cdot 10^{-3}T^2 + 0.27\cdot 10^5 T^{-1} + 51.54\,T;$$

and from 1040 to 1700°K:

$$\Delta F^\circ_T = -193{,}725 - 16.93\,T\log T + 0.61\cdot 10^{-3}T^2 - 0.94\cdot 10^5 T^{-1} + 96.81\,T.$$

The values for the free energy of formation of NbO_2 calculated from these equations are as follows:

t, °C	25	500	1000	1500
ΔF°_T, cal/mole	-177170	-156590	-136340	-117680

Niobium monoxide NbO (M = 108.91)

Crystal structure of NbO. Niobium monoxide has a face-centered cubic lattice /80, 102, 103/ where the lattice parameter a = 4.2018 kX /80/ or 4.2013 kX /103/.

Measurements of the density of niobium monoxide with the picnometric method give the value 7.15 g/cm^3. The X-ray density gives 7.26 g/cm^3 /103/.

Heat capacity of NbO. The heat content of NbO was determined by Gel'd and Kusenko /92/. These authors derived the following equation for the variation of heat capacity with temperature from their experimental data:

$$C_P = 10.04 + 2.350\cdot 10^{-3}\,T - 0.783\cdot 10^5 T^{-2}\ (1\%,\ 298\text{ to }1700°K).$$

The values calculated for C_P according to this equation are given in Table 212, those for the heat content in Table 213.

TABLE 212

Heat capacity of NbO

T, °K	C_P, cal/deg·mole	T, °K	C_P, cal/deg·mole	T, °K	C_P, cal/deg·mole
298	9.86	800	11.80	1400	13.29
400	10.49	1000	12.31	1600	13.47
600	11.23	1200	12.81	1800	14.25

Heat content of NbO. Gel'd and Kusenko /92/ derived the following equation for the heat content of NbO from their experimental data:

$$H_T - H^\circ_{298} = 10.04\,T + 1.175\cdot 10^{-3}T^2 + 0.783\cdot 10^5 T^{-1} - 3359$$

(1%, 298 to 1700°K).

Entropy of NbO. Kubaschewski and Evans /31/ give S°_{298} = 11.5 ± 1.5 cal/mole·degree.

TABLE 213

Heat content of NbO according to Gel'd and Kusenko /92/

T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole
420	1252	906	6813	1415	13264
545	2603	1008	8023	1516	14633
602	3260	1167	10103	1524	14717
730	4735	1213	10663	1700	17087
812	5657	1305	11774		

Using this value and the heat capacity equation of NbO (p. 173), we obtain

$$S^\circ_T = -46.84 + 23.12 \log T + 2.350 \cdot 10^{-3} T + 0.392 \cdot 10^5 T^{-2}.$$

The values for S°_T calculated from this equation are given below:

Temperature, °K	298	400	600	800	1000
S^0_T, cal/mole·deg	11.5	14.51	18.51	22.22	24.91
Temperature, °K	1200	1400	1600	1800	
S^0_T, cal/mole·deg	27.20	29.21	31.02	32.72	

Combining equations for $H_T - H^0_{298}$ and S°_T, we obtain the following equation for the variation of the Φ'' function with temperature:

$$\Phi'' = -56.88 + 23.12 \log T + 1.175 \cdot 10^{-3} T + 0.392 \cdot 10^5 T^{-2} + 3359/T.$$

Values for the Φ'' function, calculated from this equation, are as follows:

Temperature, °K	298	400	600	800	
Φ'', cal/mole·deg	11.5	12.40	13.77	15.44	
Temperature, °K	1000	1200	1400	1600	1800
Φ'', cal/mole·deg	17.06	18.55	19.93	21.20	22.38

Heat of formation of NbO. The following values were obtained for the heat of formation of NbO: $\Delta H^0_{298} = -108.8$ kcal/mole, Morozova and Getskina /98/; $\Delta H^0_{298} = -97.7$ kcal/mole, Kusenko and Gel'd /59/; and $\Delta H^0_{298} = -97.5$ kcal/mole, Kubaschewski and Evans /31/.

For the reaction $NbO + \frac{5}{2} O_2 = \frac{1}{2} NB_2O_5$, Morosova and Getskina /98/ give $\Delta H^0_{298} = -127.5$ kcal/mole and Kusenko and Gel'd /59/ give $\Delta H^0_{298} = -131.6$ kcal/mole. From the latter value and the heat of formation of Nb_2O_5 ($\Delta H^0_{298} = -455.2$ kcal/mole), the heat of formation of NbO, $\Delta H^0_{298} = -96.0$ kcal/mole, may be calculated. If we substitute this value for the heat of formation of NbO and use the equations given in the present reference book for the heat capacity of Nb, NbO, and O_2, we obtain the following equation for the heat of formation of NbO as a function of temperature:

$$\Delta H^\circ_T = -96,080 + 0.245 T + 0.63 \cdot 10^{-3} T^2 - 0.157 \cdot 10^5 T^{-2}.$$

The heats of formation of NbO calculated from this equation are as follows:

t, °C	25	500	1000	1500
ΔH^0_T, cal/mole	-96000	-95540	-94760	-93850

Entropy of formation of NbO. The entropy of formation of NbO for the reaction $Nb + \frac{1}{2}O_2 = NbO$, based on the values of S^0_{298} given in this reference book, may be calculated as $\Delta S^0_{298} = -21.74$ cal/mole · degree.

From the equations for ΔH°_T and ΔF°_T the following equation may be obtained:

$$\Delta S^\circ_{298} = -23.59 + 0.56 \log T + 1.26 \cdot 10^{-3} T - 0.08 \cdot 10^5 T^{-2}.$$

Free energy of formation of NbO. Using the values of ΔH^0_{298} and ΔS^0_{298} given in this reference book, we obtain $\Delta F^0_{298} = -89{,}520$ cal/mole. Using this value and $\Delta H^0_{298} = -96{,}000$ cal/mole and the heat capacities of Nb, NbO, and O_2, the following equation is obtained:

$$\Delta F^\circ_T = -96{,}080 - 0.56\, T \log T - 0.63 \cdot 10^{-3} T^2 - 0.08 \cdot 10^5 T^{-1} + 23.74\, T.$$

Values for the free energy of formation of NbO from the above equation are as follows:

t, °C	25	500	1000	1500
ΔF^0_T, cal/mole	-89520	-79365	-69100	-59020

29. HALIDES OF NIOBIUM

Niobium pentachloride $NbCl_5$ (M = 270.195)

Crystal structure of $NbCl_5$. Niobium pentachloride is monoclinic. It has the following lattice parameters: a = 18.30 Å, b = 17.96 Å, c = 5.888 Å, and β = 90.6° /19/. There are 12 molecules of $NbCl_5$ per unit cell.

Density of $NbCl_5$. According to Balke and Smith /20/, the density of $NbCl_5$ is between 2.73 and 2.77 g/cm³.

Melting point of $NbCl_5$. According to various authors /21—28/, the melting point of this compound is between 194 and 212°. Rossini /29/ gives 210°, and Kubaschewski and Evans /31/ consider 205° to be the most reliable value. The most recent value for the melting point of niobium pentachloride is 203.4° /27/.

Vapor pressure of $NbCl_5$. The normal boiling point of $NbCl_5$ is between 240 and 254° /13—28, 30/. The boiling point of niobium pentachloride at different pressures was determined by Tarasenko and Komandin /25/ and Ainscough, Holt, and Trowse /27/. Opykhtina and Fleisher /30/ used the dynamic, and Tarasenkov and Komandin /25/ and Alexander and Fairbrother /26/ used the static method. The results of various determinations are given in Table 214.

Ainscough, Holt, and Trowse /27/ report the experimental data in their paper only in the form of graphs. They derive an equation for the vapor pressure of $NbCl_5$ in the range 680 to 900 mm Hg.

$$\log P\,(\text{mm Hg}) = 8.201 - \frac{2770}{T}.$$

Schäfer, Bayer, and Lehmann /32/ made a critical evaluation of the data /25, 26, 30/ and proposed the following two equations for the vapor pressure of $NbCl_5$ (in mm Hg):

for solid $NbCl_5$:

$$\log P = -\frac{4370}{T} + 11.51;$$

and for liquid $NbCl_5$:

$$\log P = -\frac{2870}{T} + 8.37.$$

The following values were obtained from the above equations:

t, °C	130	150	170	190	210	220	230	240	250
P, mm Hg	4.7	15.1	44.7	117.5	269.2	354.8	457	603	760

TABLE 214

Vapor pressure of $NbCl_5$ according to various authors

T, °C	P, mm	Source	T, °C	P, mm	Source	T, °C	P, mm	Source
23	9	/25/	199.0	151.9	/26/	231.5	549	/25/
90	14	/25/	200.5	215.8	/30/	232	567	/25/
100	0.74	/30/	203.5	237.5	/25/	232.8	565	/25/
129.6	4.3	/26/	204.7	132.6	/26/	234	573	/25/
135	21	/25/	206.7	251	/25/	234.5	588	/25/
150.1	11.3	/26/	209.1	234.9	/26/	235.0	591	/25/
151	13.2	/30/	210.5	331.2	/30/	235.5	596	/25/
153	29	/25/	211	263	/25/	236.0	497.7	/26/
160.5	37.5	/25/	212.1	258.4	/26/	239	633	/25/
160.6	19.7	/26/	215	278	/25/	239.3	537.5	/26/
170.6	32.7	/26/	216.3	290.5	/26/	240	664	/25/
172.5	57	/25/	216.5	341	/25/	241	760	/30/
177.5	68	/25/	218	374.5	/25/	241.5	674	/25/
181	81.5	/25/	219	405	/25/	242	686	/25/
181	85.7	/30/	219.5	489.3	/30/	243.3	595.6	/26/
181.5	61.9	/26/	220.1	324.4	/26/	243.5	700	/25/
183.5	90.5	/25/	221	427	/25/	243.8	717	/25/
184.9	97.5	/25/	223.5	357.4	/26/	248.5	739	/25/
187.2	109.0	/25/	223.9	454	/25/	245	741	/25/
188.6	115.5	/25/	225	516.9	/30/	245.3	741	/25/
188.9	121.0	/25/	227	485.5	/25/	245.7	752	/25/
190.1	93.6	/26/	227.4	395.6	/26/	246	757	/25/
190.5	148.4	/30/	228	502	/25/	246.6	766	/25/
191.4	134.0	/25/	229.9	520	/25/	247	766	/25/
193	153.0	/25/	230	590	/30/	248.0	659	/26/
196.9	169.5	/25/	230.5	547	/25/	251.0	718.8	/26/
197.8	180.0	/25/	230.6	430.0	/26/	254.6	778.5	/26/
199	191.5	/25/	231.5	548	/25/			

Heats of fusion and vaporization of $NbCl_5$. According to Alexander and Fairbrother /26/, the heat of fusion of $NbCl_5$ is 7700 cal/mole at 210°.

Rossini /29/ gives L_{fus} = 8500 cal/mole (210°), and Kubaschewski and Evans /31/ L_{fus} = 6900 cal/mole (205°).

The heat of vaporization of this compound as determined by various authors is given in Table 215.

TABLE 215

Heat of vaporization of $NbCl_5$

t, °C	L_{vap} cal/mole	Author	Year	Reference
210	13200	Alexander, Fairbrother	1949	/26/
205	13100	Schäfer et al.	1952	/32/
203.4	12600	Ainscough, Holt, Trowse	1957	/27/

Rossini /29/ gives L_{vap} = 11,800 cal/mole.
For the heat of formation of $NbCl_5$, see Table 216.

TABLE 216

Heat of formation of $NbCl_5$

$-\Delta H^\circ_{298}$ kcal/mole	Author	Year	Reference
188*	Schäfer, Kahlenberg	1958	/33/
190	Schäfer	1959	/34/
190.60	Gross	1960	/35/

* Estimated value.

Niobium tetrachloride $NbCl_4$ (M = 234.722)

Schäfer and Bayer /36/ measured the vapor pressure of $NbCl_4$ at various temperatures. Measurements were carried out in the presence of $NbCl_5$ in order to eliminate disproportionation of $NbCl_4$ and the following results were obtained:

t, °C	304.2	338.3	350.1	373.9
P, mm Hg	3.8 ± 1	8.9 ± 1	18.6 ± 2	44.1

The authors derived the following equation for vapor pressure of $NbCl_4$ from 304 to 374°:

$$\log P\,(\text{mm Hg}) = 12.30 - \frac{6870}{T}.$$

The heat of sublimation of $NbCl_4$ is 31.4 kcal/mole at 304 to 374° /36/. Schäfer /35/ gives for the heat of formation of $NbCl_4$ $\Delta H^\circ_{298} = -166.0$ kcal/mole.

Disproportionation of $NbCl_4$ proceeds according to the following reaction:

$$2NbCl_4\,(s) = NbCl_3\,(s) + NbCl_5. \qquad (2)$$

According to Schäfer, Bayer, and Lehmann /32/, the vapor pressure of $NbCl_5$ in the above reaction is represented by the following equation:

$$\log P(\text{mm Hg}) = 13.16 - \frac{6190}{T} \quad (203 \text{ to } 313°)$$

from which the following values may be calculated:

t, °C	200	220	240	260	280	300	320
P, mm Hg	1.2	4.1	12.5	36	93	230	531

The free energy change for reaction (2) may be obtained from the following equation /31/:

$$\Delta F° = -RT\ln P_{NbCl_5};$$

$$\Delta F^0_T = 28{,}300 - 47.0T \quad (\pm 1 \text{ kcal}, \ 475 \text{ to } 590°K). \qquad /31/$$

Niobium oxychloride $NbOCl_3$ (M = 215.28)

The vapor pressure of $NbOCl_3$ was measured from 237 to 360° and 300 to 332° by Cherepnev /37/ and Schäfer /38/, respectively. Table 217 gives the vapor pressure of this compound in mm Hg.

TABLE 217

Vapor pressure of $NbOCl_3$

t, °C	Vapor pressure P, mm Hg		t, °C	Vapor pressure P, mm Hg	
	/37/	/38/*		/37/	/38/*
240	13.76	—	290	206	129
250	20.8	—	300	285	209
270	62.0	52.5	310	—	309
280	115.0	83	320	—	468

* Calculated from Schäfer's equation /38/.

Schäfer /38/ derived the following equation from his results on the vapor pressure of $NbOCl_3$ between 300 and 332°:

$$\log P(\text{mm Hg}) = 13.043 - \frac{6150}{T}.$$

From the above equation the sublimation temperature of $NbOCl_3$ is 332°, and the heat of sublimation is 28.1 kcal/mole at 300 to 332°. For the heat of formation of $NbOCl_3$, Schäfer /35/ gives $\Delta H^0_{298} = -210.2$ kcal/mole.

Niobium pentafluoride NbF_5 (M = 187.91)

Density of NbF_5. The density of solid NbF_5 at 18° is 3.2932 g/cm^3 (±3%). The density of liquid NbF_5 /40/ is given by the following equation:

$$d_t = 2.8026 - 9.81 \cdot 10^{-4}T - 6.16 \cdot 10^{-6}T^2.$$

Melting point of NbF_5. Values for the melting point of NbF_5, as determined by various authors, are shown in Table 218.

TABLE 218

Melting point of NbF_5

t, °C	Author	Year	Reference
75.5	Ruff, Schiller	1911	/39/
80.0	Fairbrother, Frith	1951	/40/
78.9 ± 0.2	Jenkins et al.	1952	/41/

Vapor pressure of NbF_5. The normal boiling point of this compound is between 217 and 235° /39—41/. More recent papers suggest the values 234.9° /40/ and 233.3° /41/. Table 219 presents the data of Ruff and Schiller /39/ on the vapor pressure of NbF_5.

TABLE 219

Vapor pressure of NbF_5

t, °C	P, mm Hg	t, °C	P, mm Hg	t, °C	P, mm Hg
182.0	290.0	199.5	422.6	212.5	563.2
184.5	303.1	204.5	467.1	214.5	697.2
191.6	329.7	208.4	504.7	216.5	750.4
194.5	358.9				

Fairbrother and Frith /40/ found that their experimental data from 80 to 225° can be expressed by the following equation:

$$\log P(\text{mm Hg}) = 8.439 - \frac{2824}{T}.$$

According to Jenkins et al. /41/, the vapor pressure is given by the following equations:

from 25 to 78.9°:

$$\log P(\text{mm Hg}) = 14.397 - 4900/T,$$

from 78.9 to 233°:

$$\log P(\text{mm Hg}) = 8.3716 - 2779.3/T.$$

TABLE 220

Vapor pressure of NbF_5

t, °C	Vapor pressure, P in mm Hg		t, °C	Vapor pressure, P in mm Hg		t, °C	Vapor pressure, P in mm Hg	
	/40/	/41/		/40/	/41/		/40/	/41/
25	—	0.0091	100	7.4	8.4	180	160	173
40	—	0.055	120	18	20	200	295	314
60	—	0.48	140	40	44	220	514	543
80	2.8	3.2	160	83	90	230	670	703

Table 220 gives values of the vapor pressure of NbF_5 calculated from the equation of Fairbrother and Frith /40/ and those of Jenkins et al. /41/. The results are in very good agreement with each other, but considerably lower than the old data of Ruff and Schiller.

Heats of fusion and vaporization of NbF_5. The heat of fusion of this compound is 8600 cal/mole /41/ at 78.9°. Kubaschewski and Evans /31/, using the results of Jenkins et al. /41/, calculated the following: L_{vap} = 12,500 cal/mole at 233°, L_{vap} = 14,300 cal/mole at 25°, L_{subl} = 22,400 cal/mole at 79°, and L_{subl} = 23,000 cal/mole at 25°.

Niobium pentabromide $NbBr_5$ (M = 492.49)

Crystal structure of $NbBr_5$. According to Zalkin and Lands /19/, niobium pentabromide is isomorphous with niobium pentachloride.

Melting point of $NbBr_5$. The melting point of $NbBr_5$ is 267° /31/.

Vapor pressure of $NbBr_5$. The vapor pressure of $NbBr_5$ was studied by Alexander and Fairbrother /26/ using a static method. Their data are given in Table 221.

TABLE 221

Pressure of saturated vapor of $NbBr_5$

t, °C	P mm Hg	t, °C	P mm Hg	t, °C	P mm Hg	t, °C	P mm Hg
207.5	0.5	281.8	93.8	321.2	274.6	343.1	491.7
222.3	1.8	289.5	116.7	324.1	293.6	345.5	525.6
239.9	13.9	293.6	130.2	329.1	336.4	347.3	550.4
244.1	17.6	299.9	154.9	330.7	350.4	351.1	596.7
255.7	32.4	306.5	185.5	334.2	385.5	353.5	639.3
261.1	43.9	308.5	198.3	336.4	402.5	358.3	697.8
268.7	60.5	313.5	223.5	340.0	447.3	361.7	747.6
276.8	81.6	317.2	246.5				

Alexander and Fairbrother /26/ give the following equation for the vapor pressure (mm Hg):

$$\log P = 9.33 - \frac{4085}{T}.$$

The normal boiling point of $NbBr_5$ calculated from this equation is 261°. The heat of vaporization of this compound is 18,700 cal/mole /31/.

Niobium tribromide $NbBr_3$ (M = 332.658)

When $NbBr_5$ is reduced by hydrogen at 500°, $NbBr_3$ is obtained. $NbBr_3$ decomposes at approximately 925° into Nb and $NbBr_5$ /42/.

Niobium trifluoride NbF_3 (M = 149.91)

This compound crystallizes in the cubic system, where the lattice parameter a = 3.895 kX /42/. The density of this compound, d_{25}^4, is 4.02 g/cm^3.

30. CARBIDES OF NIOBIUM

The following carbides were found in the system Nb—C by various authors: NbC /43—54/, Nb_4C_3 /55/, Nb_2C /48, 53, 56/, and Nb_4C /57/. Brauer, Renner, and Wernet /48/ report that there are two fields of homogeneity in the Nb—C system, viz., $NbC_{1.0-0.72}$, the monocarbide phase with a NaCl type lattice and the parameter a = 4.4572 to 4.4243 kX, and $NbC_{1.0-0.72}$ [sic], the subcarbide phase with a hexagonal lattice and the parameters a = 3.1198 to 3.1109 kX and c = 4.958 to 4.944 kX. A field of homogeneity of about the same width was found by Alyamovskii, Gel'd, and Shveikin /53/.

Density of NbC. According to /47/ and /45/, the density of NbC is 7.56 and 7.82 g/cm^3, respectively.

Melting point of NbC. According to Friedrich and Sittig /54/, NbC fuses at 4000 to 4100°K. Agte and Alterthum /46/ determined the melting point of NbC as 3500 ± 125°K. The presently accepted value is 3500°.

Heat content. Heat contents of the niobium carbides were measured by Gel'd and Kusenko /92/. Their data relate to carbides with the empirical formulas: $NbC_{0.50}$, $NbC_{0.749}$, $NbC_{0.867}$, and $NbC_{1.00}$, shown in Table 222. The following equations are valid for the heat contents of the above carbides from 298 to 1800°K /92/:

for $NbC_{0.50}$:

$$H_T - H^\circ_{298} = 7.94T + 0.750 \cdot 10^{-3}T^2 + 1.025 \cdot 10^5 T^{-1} - 2776;$$

for $NbC_{0.749}$:

$$H_T - H^\circ_{298} = 8.95T + 1.127 \cdot 10^{-3}T^2 + 1.26 \cdot 10^5 T^{-1} - 3190;$$

for $NbC_{0.867}$:

$$H_T - H^\circ_{298} = 9.70T + 0.995 \cdot 10^{-3}T^2 + 1.51 \cdot 10^5 T^{-1} - 3485;$$

for $NbC_{1.00}$:

$$H_T - H^\circ_{298} = 10.79T + 0.863 \cdot 10^{-3}T^2 + 2.15 \cdot 10^5 T^{-1} - 4013.$$

TABLE 222

Heat contents of the niobium carbides

$NbC_{1.00}$		$NbC_{0.867}$		$NbC_{0.749}$		$NbC_{0.50}$	
T, °K	$H_T - H^\circ_{298}$ cal/mole	T, °K	$H_T - H^\circ_{298}$ cal/mole	T, °K	$H_T - H^\circ_{298}$ cal/mole	T, °K	$H_T - H^\circ_{298}$ cal/mole
403	1020	457	1463	453	1334	410	858
534	2408	509	1999	525	2058	544	1978
602	3128	625	3212	647	3240	598	2412
697	4201	727	4336	726	4071	713	3388
805	5506	842	5575	830	5177	808	4222
895	6604	908	6312	904	5975	907	5166
992	7748	1016	7524	1041	7455	1010	5996
1105	9192	1088	8393	1085	7974	1099	6925
1199	10338	1196	9636	1190	9147	1203	7903
1292	11536	1316	11113	1291	10333	1303	8904
1402	12968	1402	12251	1401	11684	1395	9840
1500	14250	1520	13687	1511	13014	1554	11486
1790	18213	1721	16253	1763	16172	1703	12967

Gel'd and Kusenko /92/ derived the following equations for the heat capacities of these carbides:

for $NbC_{0.50}$:

$$C_p = 7.94 + 1.50 \cdot 10^{-3} T - 1.025 \cdot 10^5 T^{-2};$$

for $NbC_{0.749}$:

$$C_p = 8.95 + 2.254 \cdot 10^{-3} T - 1.26 \cdot 10^5 T^{-2};$$

for $NbC_{0.867}$:

$$C_p = 9.70 + 1.99 \cdot 10^{-3} T - 1.51 \cdot 10^5 T^{-2};$$

for $NbC_{1.00}$:

$$C_p = 10.79 + 1.726 \cdot 10^{-3} T - 2.15 \cdot 10^5 T^{-2}.$$

Values for C_P from these equations are shown in Table 223.

TABLE 223

Heat capacities of the carbides of niobium

T, °K	C_p, cal/mole · deg			
	$NbC_{0.50}$	$NbC_{0.749}$	$NbC_{0.867}$	$NbC_{1.00}$
298	7.24	8.20	8.59	8.88
400	7.90	9.06	9.55	10.14
600	8.56	9.95	10.47	11.23
800	8.98	10.56	11.06	11.83
1000	9.34	11.08	11.54	12.30
1200	9.67	11.57	11.98	12.71
1400	9.99	12.04	12.41	13.10
1600	10.30	12.51	12.83	13.47
1800	10.61	12.97	13.23	13.83

Entropy of NbC. Kubaschewski and Evans /31/ give the entropy S^0_{298} of NbC as 8.9 ± 0.7 cal/mole · degree. Gel'd and Kusenko /92/ calculated the entropies of the carbides of the composition NbC_x, assuming that S^0_{298} for NbC = 9.0 cal/mole · degree and that $\Delta S^\circ = 0$ for the reaction:

$$x\,NbC + (1-x)\,Nb = NbC_x$$

	$NbC_{0.50}$	$NbC_{0.749}$	$NbC_{0.847}$	$NbC_{1.00}$
S^0_{298}, cal/mole · deg . . .	8.74	8.86	8.93	9.0

The following equations were obtained from data on the heat contents and heat capacities of NbC and $NbC_{0.5}$ and the values $S^0_{298} = 8.9$ and $S^0_{298} = 8.6$ e.u. as the entropies of NbC and $NbC_{0.5}$, respectively:

for NbC:

$$S^\circ_T = -54.31 + 25.85 \log T + 1.726 \cdot 10^{-3} T + 1.08 \cdot 10^5 T^{-2};$$

for $NbC_{0.5}$:

$$S^\circ_T = -37.67 + 18.29 \log T + 1.50 \cdot 10^{-3} T + 0.51 \cdot 10^5 T^{-2};$$

for NbC:

$$\Phi^\circ = -85.2 + 24.85 \log T + 0.863 \cdot 10^{-3} T - 1.08 \cdot 10^5 T^{-2} + 4013 \cdot T^{-1};$$

for $NbC_{0.5}$:

$$\Phi'' = -45.61 + 18.29 \log T + 0.75 \cdot 10^{-3} T - 0.51 \cdot 10^{5} T^{-2} + 2776 \cdot T^{-1}.$$

Table 224 gives values of S_T° and Φ'' for $NbC_{0.5}$ and $NbC_{1.00}$ calculated from these equations:

TABLE 224

Entropies and Φ'' of the niobium carbides, cal/mole · deg.

T, °K	$NbC_{0.5}$		$NbC_{1.00}$		T, °K	$NbC_{0.5}$		$NbC_{1.00}$	
	S_T^0	Φ''	S_T^0	Φ''		S_T^0	Φ''	S_T^0	Φ''
298	8.6	8.6	8.9	8.9	1200	20.49	13.88	24.36	15.72
400	10.84	8.90	11.72	9.94	1400	22.00	14.99	26.35	17.10
600	14.18	10.14	16.07	10.85	1600	23.35	15.91	28.11	18.37
800	16.71	11.48	19.39	12.59	1800	24.59	16.80	29.72	19.55
1000	18.75	12.74	22.08	14.22					

Heats of formation of the niobium carbides. The heats of formation of the niobium carbides are presented in Table 225.

TABLE 225

Heats of formation of the niobium carbides

Composition	$-\Delta H_{298}^0$ kcal/mole	Author	Year	Reference
$NbC_{1.00}$	34.8	Gel'd, Kusenko	1960	/59, 92/
$NbC_{1.00}$	33.6	Mah, Boyle	1955	/58/
$NbC_{0.990}$	34.3	Gel'd, Kusenko	1960	/59, 92/
$NbC_{0.9445}$	31.75	Mah, Boyle	1955	/58/
$NbC_{0.936}$	34.0	Gel'd, Kusenko	1960	/59, 92/
$NbC_{0.877}$	33.1			
$NbC_{0.749}$	30.3			
$NbC_{0.50}$	22.71			

Table 226 gives the data of Gel'd and Kusenko /59/ on the combustion of niobium carbides of different composition. Kubaschewski and Evans /31/ give $\Delta H_{298}^0 = -33.7$ kcal/mole for the heat of formation of the carbide $NbC_{1.00}$.

We consider the following values to be the most reliable for thermodynamic calculations: $NbC_{1.00}$ $\Delta H_{298}^0 = -33$ kcal/mole, $NbC_{0.72}$ $\Delta H_{298}^0 = -28.4$ kcal/mole, and $NbC_{0.5}$ $\Delta H_{298}^0 = -21.0$ kcal/mole.

If we use the data given in this book for the heats of formation and the heat capacities of Nb, C, NbC, and $NbC_{0.5}$, the following equations are obtained:

for NbC:

$$\Delta H_T^\circ = -33{,}980 + 2.45 \cdot T - 0.927 \cdot 10^{-3} T^2 + 0.98 \cdot 10^{5} T^{-1};$$

and for $NbC_{0.5}$:

$$\Delta H_T^\circ = -21{,}400 + 0.945T - 0.385 \cdot 10^{-3}T^2 + 0.44 \cdot 10^5 T^{-1}.$$

From these equations the following values are obtained for NbC:

t, °C	25	500	1000	1500
$-\Delta H_T^0$, cal/mole	33000	32510	32290	32500

and for $NbC_{0.5}$:

t, °C	25	500	1000	1500
$-\Delta H_T^0$, cal/mole	21000	20840	20790	20960

TABLE 226

Heat of combustion of niobium carbides

Empirical formula	Phase composition	Heat of combustion $-\Delta H_{298}^0$, cal/g
$NbC_{1.422}$	$NbC_{1.00} + C_{free}$	2992.4
$NbC_{1.029}$	$NbC_{0.990} + C_{free}$	2771.4
*$NbC_{0.9445}$	$NbC_{0.9445}$	2730.1
$NbC_{0.936}$	$NbC_{0.936}$	2719.3
$NbC_{0.877}$	$NbC_{0.877}$	2693.8
$NbC_{0.749}$	$NbC_{0.749}$	2643.7
$NbC_{0.600}$	$NbC_{0.72} + NbC_{0.50}$	2594.0
$NbC_{0.530}$	$NbC_{0.72} + NbC_{0.50}$	2571.2
$NbC_{0.342}$	$NbC_{0.39} + Nb$	2528.2
$NbC_{0.170}$	$NbC_{0.39} + Nb$	2503.0

* According to Mah and Boyle / 58/.

Entropy of formation of the niobium carbides. Using the values given in this book for S_{298}^0 for Nb, C, NbC, and $NbC_{0.5}$, we obtain $\Delta S_{298}^0 = -1.20$ cal/mole · degree and $\Delta S_{298}^0 = -1.38$ cal/mole · degree for NbC and $NbC_{0.5}$, respectively.

Free energy of formation of the niobium carbides. The following values were calculated for the free energy of formation:

for NbC:

$$\Delta F_{298}^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ = -32{,}640 \text{ cal/mole},$$

and for $NbC_{0.5}$:

$$\Delta F_{298}^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ = -20{,}590 \text{ cal/mole}.$$

The free energy of formation is given by the following two equations:

for NbC:

$$\Delta F_T^\circ = -33{,}980 - 5.64T \log T + 0.927 \cdot 10^{-3}T^2 + 0.49 \cdot 10^{+5}T^{-1} + 17.79T;$$

and for $NbC_{0.5}$:

$$\Delta F_T^\circ = -21{,}400 - 2.18\,T\log T + 0.385\cdot 10^{-3}T^2 + 0.22\cdot 10^{+5}T^{-1} + 7.75T.$$

Values for the free energy of formation calculated from these equations are as follows:

for NbC:

t, °C	25	500	1000	1500
$-\Delta F_T^\circ$, cal/mole	32640	32200	31890	31890

and for $NbC_{0.5}$:

t, °C	25	500	1000	1500
$-\Delta F_T^\circ$, cal/mole	20590	20020	19310	18990

31. NITRIDES OF NIOBIUM

In the system Nb—N various authors have found the nitrides NbN /47, 56, 57, 60, 61—63/ and Nb_2N /56, 57, 62, 63/.

Crystal structure. The crystal structure of NbN is face-centered cubic /47, 57, 61, 62/ with the lattice parameter a = 4.375 Å /64/. The nitride Nb_2N has a hexagonal close packing of atoms with the following lattice parameters: a = 3.058 Å, c = 4.961 Å /56/, or a = 3.017 Å and c = 5.580 Å /57/. The density of NbN is 8.4 g/cm³ /60/. The X-ray density is 8.48 g/cm³ /64/.

Melting point of NbN. The melting point of NbN is approximately 2300°K /60/.

Heat capacity of NbN. Armstrong /66/ determined the heat capacity of NbN from 11 to 21°K.

T, °K	11.0	12.0	13.0	14.0	15.0
C_p, cal/g·deg	0.0390	0.0468	0.0612	0.0791	0.0874
T, °K	16.0	17.0	18.0	19.0	20.0
C_p, cal/g·deg	0.0848	0.0983	0.1123	0.1300	0.1535

Kelley /67/ gives the following equation for the heat capacity of NbN:

$$C_p = 8.69 + 5.40\cdot 10^{-3}T \text{ (5\%, 298 to 600°K)}.$$

The values calculated from this equation are as follows:

T, °K	300	350	400	450	500	550	600
C_p, cal/mole·deg	10.51	10.58	10.85	11.12	11.39	11.66	11.93

Heat content of NbN. From Kelley's equation /67/ for the heat capacity, the following expression is obtained for the heat content of NbN:

$$H_T - H_{298}^\circ = -2730 + 8.69T + 2.70\cdot 10^{-3}T^2.$$

The values calculated from this equation are as follows:

T, °K	400	500	600
$H_T - H_{298}^\circ$, cal/mole	1080	2190	3460

Heat of formation of NbN. Neumann, Kröger, and Kunz /65/ give $\Delta H^0_{298} = -59.0$ kcal/mole for the heat of formation of NbN. Mah and Gellert /68/ determined the heat of combustion of NbN in a calorimetric bomb and found for the reaction

$$NbN + {}^5/_4O_2 = {}^1/_2Nb_2O_5 + {}^1/_2N_2$$

$\Delta H^0_{298} = -170.83$ kcal/mole, from which the heat of formation of NbN $\Delta H^0_{298} = -56.8$ kcal/mole. Using this value and the heat capacity data for Nb, N_2, and NbN quoted in this book, we obtain the following equation:

$$\Delta H^\circ_T = -56{,}885 - 0.30T + 1.965 \cdot 10^{-3}T^2.$$

Using this equation, we obtain the following values for ΔH°_T:

T, °K	400	500	600
$-\Delta H^\circ_T$, cal/mole	55690	56540	56360

Entropy and free energy of formation. Mah and Gellert /68/ used $\Delta S^0_{298} = -22.9$ cal/mole · degree to calculate the following value: $\Delta F^0_{298} = -50.0$ kcal/mole.

32. SILICIDES OF NIOBIUM

Various authors found the following silicides in the Nb—Si system: Nb_4Si /72/, Nb_2Si /71/, Nb_5Si_3 /72, 73/, Nb_3Si_2 /73/, and $NbSi_2$ /70—72/.

Melting point. According to Wallbaum /70/, $NbSi_2$ melts below 2000°. Other authors give the melting point of $NbSi_2$ as 1950° /64/ or 1930° /72/. The compound Nb_5Si_3 melts at 2480° /72/. The density of $NbSi_2$ is 5.29 g/cm^3 /64/.

33. SULFIDES OF NIOBIUM

Hägg and Schönberg /74/ found the following sulfides in the Nb—S system: NbS with the homogeneity range $NbS_{0.9-1.2}$, and NbS_2.

34. BORIDES OF NIOBIUM

Various authors found the following borides in the Nb — B system: NbB_2 /75—79/, NbB /77, 78, 79/, Nb_3B, Nb_2B /77/, and Nb_3B_4 /77, 78/. Among them only NbB and NbB_2 are stable up to their melting points /64/. The boride NbB_2 has a hexagonal crystal structure with the parameters a = 3.086 Å and c = 3.306 Å /64/. The boride NbB has an orthorhombic structure with the following lattice parameters: a = 3.298 Å, b = 8.729 Å, c = 3.166 Å.

Density of boride NbB_2. The density of NbB_2 is 6.60 g/cm^3. Another source /75/ gives d_{15} = 6.4 g/cm^3. The X-ray density of NbB_2 is 7.21 g/cm^3 /64/.

Melting point of NbB_2. The melting point of NbB_2 is approximately 2900° /64/.

35. HYDRIDES OF NIOBIUM

Various hydrides of niobium were obtained by various authors, both by direct treatment of metallic niobium with molecular or atomic hydrogen at elevated temperatures /5, 190, 191, 192, 193, 194, 195/, and by the effect of various reducing agents on niobium halides or oxides /196, 198/. Other methods include electrolysis of sulfuric acid using a niobium cathode /8/ and reaction of metallic niobium with a 10% solution of hydrofluoric acid in aqueous medium /197/.

Marignac /196/ was the first to obtain niobium hydride of 1.2% hydrogen content (by weight), corresponding to the formula $NbH_{1.2}$. He considered this hydride to be the compound NbH (see also /57, 62, 199/). Muthmann, Weiss, and Riedelbauch /5/ were of the opinion that the hydrogen in the hydride was not bound to niobium in stoichiometric proportions.

Several workers studied the crystal structure of this niobium hydride by means of X-ray analysis. Umanskii /57/ suggested for NbH a face-centered cubic lattice with rhombic distortion with the lattice parameter a = 3.42 Å. Ascherman et al. /62/, however, found a face-centered crystal lattice for NbH. Many authors /210, 215, 216, 217/ showed that in the Nb—H system at room temperature there are two solid homogeneous phases of variable composition with a two-phase region between them.

1. α-phase-homogeneous solid solution of H in Nb (hydrogen content between 0 and 10 at. % H), corresponding to the formula $NbH_{0.11}$ /209, 210/ or $NbH_{0.091}$ /215/. Trzebiatowski and Stalinski /216, 217/ observed that for solid solutions of hydrogen in niobium the lattice constant increases from 3.303 to 3.318 Å, the lattice figure corresponding to the composition $NbH_{0.10}$.

2. Brauer and Hermann /210/ found that the heterogeneous region ($\alpha+\beta$) extends from $NbH_{0.11}$ to $NbH_{0.78}$. Knowles /215/ reports the existence of a two-phase region between $NbH_{0.09}$ and $NbH_{0.85}$, while Trzebiatowski and Stalinski /216, 217/ report this two-phase region to exist between $NbH_{0.10}$ and $NbH_{0.57}$.

3. β-phase — the second homogeneity region. It starts from a compound corresponding to the formula $NbH_{0.70}$ /210/, $NbH_{0.83}$ /215/, or $NbH_{0.57}$ /216, 217/.

The hydrogen content in the β-phase increases up to the composition $NbH_{0.89}$ /210/ or $NbH_{0.86}$ /216, 217/. Brauer and Hermann /210/ report that the compound $NbH_{0.89}$ has an orthorhombic lattice with the following lattice parameters: a = 4.84 Å, b = 4.90 Å, and c = 3.45 Å.

Sieverts and Hagen /192, 193/ determined isotherms and isobars for the solubility of hydrogen in niobium. They determined the solubility of hydrogen in niobium from 20 to 900° at a constant pressure 760 mm Hg (Table 227). According to the data of Sieverts /192, 193/ the isotherm obeys the square root law at 500°. For the isotherms at 300 and 400° no such relation was found. Perminov /194/ studied the influence of pressure on the solubility of hydrogen in niobium from 620 to 680°. He found that absorption of hydrogen in the composition range $NbH_{0.53}$ to $NbH_{0.73}$ also obeys the square root law. Gulbransen and Andrew /190, 191/ studied the kinetics of hydrogenation of niobium and the stability of the resultant hydrogenated phases. They found that the rate of absorption is fairly high between 250 and 360°. It decreases with increasing temperature up to 580°. This phenomenon is probably due to decomposition of low-temperature form of the

hydride. The latter is stable at a pressure of 10^{-6} mm Hg up to 250°, but decomposes at higher temperatures. Absorption of hydrogen by niobium between 560 and 900° indicates that a more stable hydride is formed at higher temperatures. This hydride is stable in high vacuum (10^{-6} mm Hg) up to 1100°; at higher temperatures it decomposes.

TABLE 227

Solubility of hydrogen in niobium

t, °C	Amount of absorbed hydrogen (cm^3H_2/ g Nb)	t, °C	Amount of absorbed hydrogen (cm^3H_2/ g Nb)
20	(104)	500	47.4
200	(93.3)	550	29.7
300	88.0	600	18.5
350	83.6	700	9.7
400	76.8	800	6.1
450	65.6	900	4.0

Note: Values in brackets were obtained by extrapolation.

Albrecht, Mallet, and Goode /218/ studied the Nb—H system at 100 to 900° and 10 to 1000 mm Hg in the range N_{Nb} = 0.01 to 0.85. The heat of formation of $NbH_{0.60}$ as determined by these authors was −20,610 cal/mole.

The density of NbH is ~ 6.0 to 6.6 g/cm^3 according to Marignac /196/.

TABLE 228

Heat capacity of NbH

Temperature range, °C	Average specific heat capacity C_p, cal/g·deg	Average molar heat capacity C_p, cal/mole·deg
0—100	0.0980—0.0987	9.3
0—210.5	0.0927—0.0923	8.8
0—301.5	0.0870—0.0871	8.3
0—440	0.0833—0.0835	7.9

The heat capacity of NbH was determined by Krüss and Nilson /199/. It decreases with increasing temperature, which can be explained by the fact that hydrogen is split off at increased temperatures so that the composition of the hydride changes. The data of Krüss and Nilson /199/ are shown in Table 228.

Chapter 6

THERMODYNAMIC PROPERTIES OF TANTALUM AND OF ITS MORE IMPORTANT COMPOUNDS

36. METALLIC TANTALUM (M = 180.88)

Crystal structure, melting point, vapor pressure

No data are available on the polymorphism of tantalum.

Crystal structure of tantalum. Metallic tantalum has a body-centered cubic (Na-type) lattice with the lattice parameter a_0 = 3.2959 ± 0.0003 kX at 20° /1/. Edwards, Speiser, and Johnston /106/ measured the lattice parameters at 18° and from 862 to 2222°, and derived the following equation:

$$a_{0,T} = a_0 [1 + 6.080 \cdot 10^{-6} (T-291) + 7.50 \cdot 10^{-10} (T-291)^2],$$

where a_0 is the lattice parameter at 291°K.

The density of tantalum is 16.64 g/cm^3 at 19.6° /107/. (Cf. also /1, 5, 8, 108, 110 to 113, 116/).

Coefficient of linear expansion of tantalum. The following coefficients of linear expansion of tantalum from 0 to 1500° are given by Goetzel /3/:

Temperature range, °C	0—100	0—200	0—300	0—400	0—500	0—600
$\alpha \cdot 10^6$	6.5	6.5	6.5	6.5	6.6	6.6

Temperature range, °C	0—700	0—800	0—900	0—1000	20—1500
$\alpha \cdot 10^6$	6.6	6.6	6.6	6.6	8.0

The data of Goetzel /3/ show fairly good agreement with those of Worthing /114/ and of Edwards, Speiser, and Johnston /106/ (see also /115/).

Melting point of tantalum. In older references /114, 118, 119, 120, 121, 122/, the melting point of Ta is given as between 2800 and 3000°. Goetzel /3/ determined the melting point of Ta as 2996°; the same temperature is given by Martini /117/. Stull and Sinke /18/ and Rossini /29/ give the value 2977°.

Vapor pressure of tantalum. The normal boiling point of tantalum is 5300°. This value was determined by Mott /121/, using the optical method. The same value is given by Goetzel /3/ and Stull and Sinke /18/. Martini /117/ gives the boiling point of tantalum at 760 mm Hg as 6027°; Kubaschewski /31/ as 6100°.

Edwards, Johnston, and Blackburn /130/ measured the vapor pressure of tantalum between 2624 and 2943°K using the Langmuir method. Their results showed good agreement with those of Langmuir and Malter /124/, but differ from the results obtained by Fiske /125/. Edwards, Johnston, and Blackburn /130/ give the following equation for the vapor pressure of tantalum:

$$R \ln P = -185.5 \cdot 10^3 T^{-1} + 3.7 \cdot 10^{-4} T - 8.4 \cdot 10^{-8} T^2 + 32.87.$$

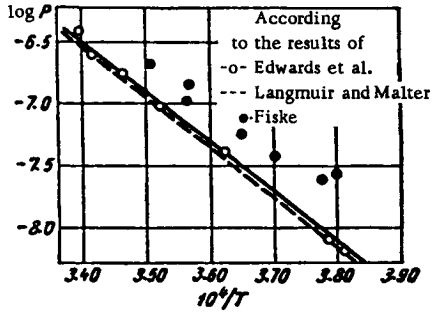

Figure 6. Vapor pressure of tantalum.

Table 229 gives experimental results of the three papers mentioned above /124, 125, 130/; for the sake of comparison, these results have been plotted in Figure 6.

TABLE 229

Vapor pressure of tantalum

T, °K	P, atm. /130/	-RlnP, cal/mole·deg /130/	/124/	/125/	T, °K	P, atm. /130/	-RlnP, cal/mole·deg /130/	/124/	/125/
2000	—	—	59.08	—	2800	—	—	33.09	—
2200	—	—	50.85	—	2804	—	—	—	31.33
2400	—	—	43.94	—	2807	—	—	—	31.09
2600	—	—	38.09	—	2839	$9.692 \cdot 10^{-8}$	32.09	—	—
2624	$6.216 \cdot 10^{-9}$	37.55	—	—	2850	—	—	—	30.59
2633	—	—	—	34.80	2888	$1.698 \cdot 15^{-7}$	30.98	—	—
2638	$7.390 \cdot 10^{-9}$	37.21	—	—	2925	$2.408 \cdot 10^{-7}$	30.28	—	—
2649	—	—	—	34.85	2948	$3.655 \cdot 10^{-7}$	29.45	—	—
2700	—	—	—	33.94	3000	—	—	28.71	—
2737	—	—	—	33.12	3200	—	—	24.90	—
2760	$3.966 \cdot 10^{-8}$	33.87	—	—					

Heat capacity, heat of fusion, and heat of sublimation

Heat capacity of tantalum. The heat capacity of tantalum was determined by Worley, Zemansky, and Boorse /126/ from 1.7 to 5°K, by Keesom and Desirant /127/ from 1.3 to 4.8°K, and by Sterrett and Wallace /128/ from 12 to 550°K. Kelley /129/ determined the heat capacity of tantalum from 53 to 298°K; and Simon and Ruheman /131/ from 71 to 78°K.

TABLE 230

True heat capacity of solid tantalum

Temperature, °K	Heat capacity		Author	Reference
	specific, cal/g-deg	atomic, cal/g-at-deg		
12	—	0.074		
14	—	0.0115		
15	—	0.143		
16	—	0.175		
18	—	0.250		
20	—	0.338		
22	—	0.443		
24	—	0.564	Sterrett, Wallace	/128/
25	—	0.631		
26	—	0.703		
28	—	0.857		
30	—	1.006		
35	—	1.411		
40	—	1.824		
45	—	2.228		
50	—	2.592		
53	—	2.81	Kelley	/129/
55	—	2.936	Sterrett, Wallace	/128/
55	—	2.95	Kelley	/129/
60	—	3.245	Sterrett, Wallace	/128/
60	—	3.26	Kelley	/129/
65	—	3.520	Sterrett, Wallace	/128/
65	—	3.54	Kelley	/129/
70	—	3.755	Sterrett, Wallace	/128/
70	—	3.80	Kelley	/129/
71.11	—	3.56		
71.44	0.0197	3.57	Simon, Ruheman	/131/
71.74	—	3.59		
75	—	3.972	Sterrett, Wallace	/128/
75	—	4.03	Kelley	/129/
77.50	—	3.81		
77.82	0.0205	—	Simon, Ruheman	/131/
77.90	—	3.84		
80	—	4.170	Sterrett, Wallace	/128/
80	—	4.22	Kelley	/129/
85	—	4.348	Sterrett, Wallace	/128/
85	—	4.40	Kelley	/129/
90	—	4.499	Sterrett, Wallace	/128/
90	—	4.55	Kelley	/129/
95	—	4.623	Sterrett, Wallace	/128/
95	—	4.68	Kelley	/129/
100	—	4.737	Sterrett, Wallace	/128/
100	—	4.78	Kelley	/129/
105	—	4.841	Sterrett, Wallace	/128/
105	—	4.87	Kelley	/129/
110	—	4.941	Sterrett, Wallace	/128/
110	—	4.97	Kelley	/129/
115	—	5.206	Sterrett, Wallace	/128/
115	—	5.06	Kelley	/129/
120	—	5.106	Sterrett, Wallace	/128/
120	—	5.14	Kelley	/129/
125	—	5.177	Sterrett, Wallace	/128/

TABLE 230 (Continued)

Temperature, °K	Heat capacity		Author	Reference
	specific, cal/g·deg	atomic, cal/g·at·deg		
130	—	5.242	Sterrett, Wallace	/128/
130	—	5.27	Kelley	/129/
135	—	5.302	Sterrett, Wallace	/128/
135	—	5.33	Kelley	/129/
140	—	5.360	Sterrett, Wallace	/128/
140	—	5.39	Kelley	/129/
145	—	5.404	Sterrett, Wallace	/128/
145	—	5.44	Kelley	/129/
150	—	5.449	Sterrett, Wallace	/128/
150	—	5.48	Kelley	/129/
155	—	5.492	Sterrett, Wallace	/128/
155	—	5.52	Kelley	/129/
160	—	5.533	Sterrett, Wallace	/128/
160	—	5.55	Kelley	/129/
165	—	5.569	Sterrett, Wallace	/128/
165	—	5.58	Kelley	/129/
170	—	5.603	Sterrett, Wallace	/128/
170	—	5.62	Kelley	/129/
175	—	5.633	Sterrett, Wallace	/128/
175	—	5.65	Kelley	/129/
180	—	5.661	Sterrett, Wallace	/128/
180	—	5.68	Kelley	/129/
185	—	5.689	Sterrett, Wallace	/128/
185	—	5.70	Kelley	/129/
190	—	5.715	Sterrett, Wallace	/128/
190	—	5.73	Kelley	/129/
195	—	5.739	Sterrett, Wallace	/128/
195	—	5.76	Kelley	/129/
200	—	5.761	Sterrett, Wallace	/128/
200	—	5.78	Kelley	/129/
205	—	5.783	Sterrett, Wallace	/128/
205	—	5.80	Kelley	/129/
210	—	5.804	Sterrett, Wallace	/128/
210	—	5.82	Kelley	/129/
215	—	5.882	Sterrett, Wallace	/128/
215	—	5.84	Kelley	/129/
220	—	5.839	Sterrett, Wallace	/128/
220	—	5.86	Kelley	/129/
225	—	5.855	Sterrett, Wallace	/128/
225	—	5.88	Kelley	/129/
230	—	5.872	Sterrett, Wallace	/128/
230	—	5.89	Kelley	/129/
235	—	5.888	Sterrett, Wallace	/128/
235	—	5.91	Kelley	/129/
240	—	5.903	Sterrett, Wallace	/128/
240	—	5.92	Kelley	/129/
245	—	5.917	Sterrett, Wallace	/128/
245	—	5.94	Kelley	/129/
250	—	5.931	Sterrett, Wallace	/128/
250	—	5.95	Kelley	/129/
255	—	5.943	Sterrett, Wallace	/128/

TABLE 230 (continued)

Temperature, °K	Heat capacity		Author	Reference
	specific, cal/g-deg	atomic, cal/g-at-deg		
255	—	5.96	Kelley	/129/
260	—	5.955	Sterrett, Wallace	/128/
260	—	5.98	Kelley	/129/
265	—	5.967	Sterrett, Wallace	/128/
265	—	5.99	Kelley	/129/
270	—	5.980	Sterrett, Wallace	/128/
270	—	6.01	Kelley	/129/
273.16	—	5.987	Sterrett, Wallace	/128/
273.16	0.0322	6.024	Jaeger, Veenstra	/8/
273.16	—	6.174	Magnus, Holzmann	/132/
275	—	5.992	Sterrett, Wallace	/128/
275	—	6.02	Kelley	/129/
280	—	6.005	Sterrett, Wallace	/128/
280	—	6.03	Kelley	/129/
285	—	6.017	Sterrett, Wallace	/128/
285	—	6.03	Kelley	/129/
290	—	6.029	Sterrett, Wallace	/128/
290	—	6.04	Kelley	/129/
295	—	6.039	Sterrett, Wallace	/128/
295	—	6.04	Kelley	/129/
298.16	—	6.045		
300	—	6.049		
305	—	6.058		
310	—	6.067		
315	—	6.075		
320	—	6.084		
325	—	6.092		
330	—	6.100		
335	—	6.109	Sterrett, Wallace	/128/
340	—	6.117		
345	—	6.126		
350	—	6.135		
355	—	6.144		
360	—	6.152		
365	—	6.160		
370	—	6.167		
373	0.03364	6.101	Jaeger, Veenstra	/8/
373	—	6.275	Magnus, Holzmann	/132/
375	—	6.173	Sterrett, Wallace	/128/
380	—	6.179		
385	—	6.185		
390	—	6.191		
395	—	6.197		
400	—	6.203		
405	—	6.209		
410	—	6.216	Sterrett, Wallace	/128/
415	—	6.222		
420	—	6.229		
425	—	6.236		
430	—	6.244		
435	—	6.252		
440	—	6.259		

TABLE 230 (continued)

Temperature, °K	Heat capacity		Author	Reference
	specific, cal/g·deg	atomic, cal/g·at·deg		
445	—	6.266	Sterrett, Wallace	/128/
450	—	6.274		
455	—	6.282		
460	—	6.289		
465	—	6.296		
470	—	6.304		
473	0.03407	6.179	Jaeger, Veenstra	/8/
473	—	6.376	Magnus, Holzmann	/132/
475	—	6.311	Sterrett, Wallace	/128/
480	—	6.318		
485	—	6.326		
490	—	6.334		
495	—	6.341		
500	—	6.348		
505	—	6.355		
510	—	6.362		
515	—	6.368		
520	—	6.375		
525	—	6.382		
530	—	6.390		
535	—	6.397		
540	—	6.404		
543.16	—	6.408		
573	0.03450	6.257	Jaeger, Veenstra	/8/
573	—	6.477	Magnus, Holzmann	/132/
653	0.035	6.4	Pirani	/133/
673	0.03495	6.339	Jaeger, Veenstra	/8/
673	—	6.578	Magnus, Holzmann	/132/
773	0.03540	6.420	Jaeger, Veenstra	/8/
773	—	6.679	Magnus, Holzmann	/132/
873	0.03585	6.502	Jaeger, Veenstra	/8/
873	—	6.780	Magnus, Holzmann	/132/
973	0.034	6.2	Pirani	/133/
973	0.03632	6.587	Jaeger, Veenstra	/8/
1073	0.03679	6.672		
1073	—	6.982	Magnus, Holzmann	/132/
1173	0.036	6.5	Pirani	/133/
1173	0.03726	6.757	Jaeger, Veenstra	/8/
1173	—	7.082	Magnus, Holzmann	/132/
1273	0.03774	6.844	Jaeger, Veenstra	/8/
1373	0.043	7.8	Pirani	/133/
1373	0.03823	6.933	Jaeger, Veenstra	/8/
1473	0.03873	7.024		
1573	0.03923	7.115		
1673	0.0435	7.89	Pirani	/133/
1673	0.03974	7.207	Jaeger, Veenstra	/8/
1773	0.04026	7.302		
1873	0.04078	7.401		

The heat capacity of tantalum at high temperatures was determined by the following workers: Jaeger and Veenstra /8/ (from 273 to 1828°K), Magnus and Holzmann /132/ (from 273 to 1173°K), and Pirani /133/ (from 673 to 1673°K).

The results of Simon and Ruheman /131/ are apparently not accurate; they are about 8% lower than those of Kelley /129/, which show very good agreement with the more recent data of Sterrett and Wallace /128/. Experimental data on the heat capacities of tantalum above 298°K, obtained by the latter authors /128/, agree to within ± 3% with those of Jaeger and Veenstra /8/ and Magnus and Holzmann /132/. Table 230 contains data of the above authors on the specific and atomic heat capacities of solid tantalum from 12°K to 1873°.

Stull and Sinke /18/ report values for the atomic heat capacity of tantalum from 298 to 3000°K (see Table 232).

Table 231 shows the average specific and atomic heat capacities of solid tantalum as determined by various authors.

TABLE 231

Average heat capacity of solid tantalum

Temperature, °C		Heat capacity		Author	Reference
t_1	t_2	specific cal/g·deg	atomic cal/g·at·deg		
—	—	0.0346	6.32	Muthmann, Weiss, Riedelbauch	/5/
-185	+20	0.0326	5.92	Nordmeyer, Bernoulli	/134/
-183	-78	0.028	5.1		
-78	+14	0.032	5.8	Siemens	/135/
+14	+100	0.033	6.0		
+16	+100	0.0363	6.64	Bolton	/136/

Jaeger and Veenstra /8/ derived the following equation from their results (from 273 to 1828°K, 1% accuracy):

$$C_p = 5.79 + 0.825 \cdot 10^{-3} T.$$

The following values are obtained from this equation:

t, °C	25	100	500	900	1500
C_p, cal/g·atom·deg	6.04	6.10	6.43	6.76	7.25

Magnus and Holzmann /132/ derived the following equation from their data (from 273 to 1173°K, 2% accuracy):

$$C_p = 5.91 + 0.99 \cdot 10^{-3} T.$$

The following values are obtained from this equation:

t, °C	25	100	500	900
C_p, cal/g·atom·deg	6.21	6.28	6.67	7.07

Kelley /17/ used the data of Jaeger and Veenstra /8/, Magnus and Holzmann /132/, and Pirani /133/ and derived the following equation for the heat capacity of solid titanium:

$$C_p = 5.82 + 0.78 \cdot 10^{-3} T \text{ (1\%, 298 to 1900°K).}$$

The following values are obtained from this equation:

t, °C	25	100	500	1000	1600
C_p, cal/g·atom·deg	5.84	5.90	6.21	6.60	7.068

The basic thermodynamic values of solid tantalum as given by Stull and Sinke /18/ are shown in Table 232.

TABLE 232

Basic thermodynamic values for solid tantalum according to Stull and Sinke /18/

T, °K	C_P cal/mole·deg	$H_T^0 - H_{298}^0$ cal/mole	S_T^0 cal/mole·deg	$\Phi^* = -\frac{F_T^0 - H_{298}}{T}$ cal/mole·deg
298	6.08	0	9.90	9.90
300	6.08	11	9.94	9.91
400	6.27	629	11.71	10.14
500	6.38	1260	13.13	10.61
600	6.46	1900	14.30	11.14
700	6.52	2550	15.30	11.66
800	6.57	3210	16.17	12.16
900	6.63	3870	16.95	12.65
1000	6.67	4530	17.65	13.12
1100	6.72	5200	18.29	13.57
1200	6.76	5880	18.87	13.97
1300	6.81	6550	19.42	14.39
1400	6.85	7240	19.92	14.75
1500	6.90	7930	20.40	15.12
1600	6.94	8620	20.84	15.46
1700	6.98	9310	21.26	15.79
1800	7.02	10010	21.66	16.10
1900	7.07	10720	22.04	16.40
2000	7.11	11430	22.41	16.70
2100	7.15	12140	22.76	16.98
2200	7.19	12860	22.09	17.25
2300	7.23	13580	23.41	17.51
2400	7.28	14300	23.72	17.77
2500	7.32	15030	24.02	18.01
2600	7.36	15770	24.31	18.25
2700	7.40	16510	24.58	18.47
2800	7.44	17250	24.85	18.69
2900	7.48	17990	25.11	18.91
3000	7.53	18740	25.37	19.13

Heat of fusion of tantalum. Kubaschewski and Evans /31/ give the heat of fusion of tantalum at its melting point 2980° as 5900 ± 700 cal/g·atom. Stull and Sinke give L_{fus} = 7500 cal/g·atom at 2997°.

Heat of sublimation of tantalum. From vapor pressure measurements on solid tantalum, Edwards, Johnston, and Blackburn /130/ calculated the heat of sublimation of this element at absolute zero as 185.5 ± 0.3 kcal/mole. This value shows good agreement with the value 185.4 ± 0.3 kcal/mole obtained from the data of Langmuir and Malter /124/ on the rate of evaporation of tantalum, but differs slightly from the value 181.2 ± 0.9 kcal/mole calculated from the less accurate data of Fiske /125/.

The following values for the heat of sublimation of tantalum in kcal/mole at 25° are given in various reference books: Rossini et al. /29/, 185.0; Kubaschewski and Evans /31/, 183.9 ± 5 (at 6100°, 189.8 ± 7); Stull and Sinke /18/, 186.8 (at 5327°, 180.0).

Heat content and entropy of tantalum, free energy function

Heat content of tantalum. Sterrett and Wallace /128/ calculated the heat content of solid tantalum from heat capacity data on this metal by graphic interpolation. They obtained the following values:

Temperature, °K	273.16	298.16	543.16
$H_T - H^\circ_0$, cal/g·atom	1207 ± 1	1358 ± 1	2885 ± 3

The following expression for solid tantalum was obtained from Kelley's equation /17/:

$$H_T - H^\circ_{298} = 5.82\,T + 0.39 \cdot 10^{-3} T^2 - 1770 \ (1\%;\ 298 \text{ to } 1900^\circ).$$

The values for $H_T - H^0_{298}$, given in the reference book of Stull and Sinke /18/, are shown in Table 232.

Entropy of tantalum. Table 233 contains values for S^0_{298} obtained from heat capacity data of solid tantalum by graphic integration and extrapolation to 0°K.

TABLE 233

Entropy of tantalum

S^0_{298}	Author	Reference	Year
9.9 ± 0.1	Kelley	/129/	1940
9.90 ± 0.02	Clusius, Losa	/127/	1955
9.92 ± 0.01	Sterrett, Wallace	/128/	1958

The following values for S^0_{298} are given in various reference books (cal/mole·degree): Rossini et al. /29/, 9.9; Kelley /17/, 9.94 ± 0.1; Stull and Sinke /18/, 9.90.

Values for the entropy of solid tantalum [at other temperatures than 298°K], as given by Stull and Sinke /18/, are shown in Table 232.

The Φ' and Φ'' functions. Edwards, Johnston, and Blackburn /130/ give the following equation for the Φ' function:

$$\Phi' = -\frac{559}{T} + 9.773 \cdot 10^{-4} T + 9.6591 \log T - 17.26.$$

The authors used this equation for the calculation of the Φ' function at various temperatures:

Temperature, °K	2624	2638	2760	2839	2888	2925	2948
Φ', cal/mole·deg	18.12	18.15	18.47	18.67	18.80	18.89	18.94

Table 232 contains the values of the function $\Phi'' = -\frac{F^\circ_T - H^0_{298}}{T}$, as given by Stull and Sinke /18/.

Tantalum, considered as an ideal monatomic gas. Table 234 shows the basic thermodynamic values of tantalum considered as an ideal monatomic gas, as calculated by Stull and Sinke /18/. For

their calculations the authors used the static method and the spectroscopic data of Van den Berg, Klinkenberg, and Van den Bosch /138/ (Table 234).

TABLE 234

Thermodynamic values of monatomic gaseous tantalum
(Stull and Sinke /18/)

T, °K	C_P cal/mole·deg	$H_T^0 - H_{298}^0$ cal/mole	S_T^0 cal/mole·deg	$\frac{\Phi = -(F_T^0 - H_{298}^0)}{T}$ cal/mole·deg	Formation of Ta (s), cal/mole	
					$\Delta H°$	$\Delta F°$
298	4.99	0	44.24	44.24	186800	176561
300	4.99	9	44.27	44.24	186798	176499
400	5.08	512	45.72	44.44	186683	173079
500	5.28	1029	46.87	44.82	186569	169698
600	5.54	1570	47.86	45.25	186470	166334
700	5.83	2138	48.73	56.68	186388	162987
800	6.11	2735	49.53	46.12	186325	159637
900	6.38	3359	50.26	46.53	186289	156310
1000	6.62	4009	50.95	46.95	186279	152979
1100	6.84	4683	51.59	47.34	186283	149653
1200	7.04	5377	52.19	47.71	186297	146313
1300	7.22	6091	52.77	48.09	186341	142986
1400	7.38	6821	53.31	48.44	186381	139635
1500	7.51	7565	53.82	48.78	186435	136305
1600	7.63	8322	54.31	49.11	186502	132950
1700	7.73	9090	54.77	49.43	186580	129613
1800	7.82	9867	55.22	49.74	186657	126249
1900	7.89	10653	55.64	50.04	186733	122893
2000	7.96	11446	56.05	50.33	186816	119536
2100	8.02	12245	56.44	50.61	186905	116117
2200	8.08	13050	56.81	50.88	186990	112806
2300	8.13	13861	57.17	51.15	187081	109433
2400	8.18	14676	57.52	51.41	187176	106056
2500	8.22	15496	57.86	51.67	187266	102666
2600	8.26	16319	58.18	51.91	187349	99287
2700	8.29	17147	58.49	52.14	187437	95880
2800	8.32	17977	58.79	52.37	187527	92496
2900	8.35	18811	59.09	52.61	187621	89079
3000	8.38	19648	59.37	52.83	187708	85708

37. OXIDES OF TANTALUM

Various authors found the following oxides in the tantalum-oxygen system: Ta_2O /139/, TaO_2 /54, 136, 140/, and Ta_2O_5. Only the existence of the last compound has been verified. Tantalum pentoxide occurs in at least three modifications /139, 141, 142/. The transition temperatures of these modifications have not been accurately determined. The data of various authors show appreciable differences.

Tantalum pentoxide Ta_2O_5 (M = 441.9)

Density of Ta_2O_5. According to various authors the density of Ta_2O_5 is between 7.35 and 8.62 g/cm^3 /143–144/.

Melting point of Ta_2O_5. Tantalum pentoxide fuses at 1469°, 1875°, and 1620°, according to /145/, /146/, and /147/, respectively. Rossini et al. /29/ give 1890°.

Heat capacity of Ta_2O_5. The heat capacities of Ta_2O_5 at low temperatures were determined by Kelley /148/. His results are given in Table 235.

TABLE 235

Heat capacity of Ta_2O_5

T, °K	C_p cal/mole·deg	T, °K	C_p cal/mole·deg	T, °K	C_p cal/mole·deg
53.4	5.872	115.7	16.19	214.2	26.88
57.6	6.623	124.9	17.49	224.5	27.71
62.1	7.480	134.9	18.86	234.7	28.54
66.6	8.353	145.0	20.10	245.2	22.34
70.9	9.142	154.7	21.23	255.8	30.15
75.4	9.971	165.0	22.33	265.8	30.65
81.5	10.93	174.6	23.34	275.5	31.14
86.2	11.70	184.4	24.29	285.0	31.76
95.6	13.12	194.6	25.20	294.2	32.10
105.3	14.70	203.4	26.04		

Orr /90/ measured the heat content of solid Ta_2O_5. The following equation can be derived from his results on the heat capacity from 298 to 1800°K.

$$C_p = 37.00 + 6.56 \cdot 10^{-3} T - 5.92 \cdot 10^{5} T^{-2}.$$

Values for the heat capacity calculated from this equation are given below:

Temperature, °K	298	400	600	800
C_p, cal/mole·deg	33.06	35.92	39.30	41.32
Temperature, °K	1000	1200	1400	1600	1800
C_p, cal/mole·deg	42.97	44.46	45.88	47.27	48.63

The heat content of Ta_2O_5 according to Orr is given in Table 236.

TABLE 236

Heat content of Ta_2O_5, according to Orr /90/

T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole	T, °K	$H_T - H^0_{298}$ cal/mole
395.6	3270	884.9	22650	1394.2	45090
488.4	6590	988.8	27150	1497.8	49860
596.5	10850	1083.6	31310	1590.3	54060
693.6	14750	1173.7	35260	1678.2	58340
787.9	18620	1285.2	40250	1802.6	64440

Heat content of Ta_2O_5. Orr /90/ derived the following equation on the heat content of Ta_2O_5 from his experimental results (from 298 to 1800°K):

$$H_T - H^0_{298} = 37.00T + 3.28 \cdot 10^{-3} T^2 + 5.92 \cdot 10^{5} T^{-1} - 13,309.$$

The values calculated by this equation are presented below:

Temperature, °K	400	600	800	1000
$H_T - H^0_{298}$, cal/mole	3430	10,950	19,130	27,630
Temperature, °K	1200	1400	1600	1800
$H_T - H^0_{298}$, cal/mole	36,410	45,390	54,630	64,220

Entropy of Ta_2O_5. Kelley /148/ calculated the standard entropy of this compound from heat capacity values at low temperatures and obtained $S^0_{298} = 34.2 \pm 0.4$ cal/mole·degree. This value is the sum of 31.36 cal/mole·degree calculated by graphic integration, and 2.83 cal/mole·degree obtained by extrapolation from 53.1°K to 0°K.

If we use Orr's equation /90/ for C_P, we obtain the following expression for the entropy of Ta_2O_5 (298 to 1800°K):

$$S^\circ_T = -181.9 + 85.21 \log T + 6.56 \cdot 10^{-3} T + 2.96 \cdot 10^5 T^{-2}.$$

The values for S°_T calculated from this equation are given below:

Temperature, °K	298	400	600	800	
S^0_T, cal/mole·deg	34.2	44.28	59.58	71.17	
Temperature, °K	1000	1200	1400	1600	1800
S^0_T, cal/mole·deg	80.58	88.55	95.50	101.73	107.37

Combining the equations for $H_T - H^0_{298}$ and S°_T, we obtain the following expression for the Φ'' function (298 to 1800°K):

$$\Phi'' = -\frac{F^\circ_T - H^\circ_{298}}{T} = \frac{H_T - H^\circ_{298}}{T} + S^\circ_T.$$

$$\Phi'' = -218.91 + 85.21 \log T + 3.28 \cdot 10^{-3} T - 2.96 \cdot 10^5 T^{-2} + 13{,}309 T^{-1}.$$

Values for the Φ'' function calculated from this equation are presented below:

Temperature, °K	298	400	600	800	
Φ'', cal/mole·deg	34.2	35.54	41.15	47.26	
Temperature, °K	1000	1200	1400	1600	1800
Φ'', cal/mole·deg	53.01	59.29	63.12	67.56	71.67

Heat of formation of Ta_2O_5. Table 237 contains the data of various authors for the heat of formation of tantalum pentoxide. These were obtained from combustion of metallic tantalum in a calorimetric bomb according to the reaction $2Ta + \frac{5}{2}O_2 \rightarrow Ta_2O_5$:

TABLE 237

Heat formation of Ta_2O_5

$-\Delta H^0_{298}$ kcal/mole	Author	Year	Reference
498.3	Moorse, Parr	1924	/151/
480.5	Sieverts, Gotta	1930	/152/
486.0	Becker, Roth	1933	/96/
499.0	Neumann, Kröger, Kunz	1934	/65/
488.8	Humphrey	1951	/153/
480.0	Smirnova, Ormont	1955	/165/

Rossini /29/ gives $\Delta H^0_{298} = -499.9$ kcal/mole. Kubaschewski and Evans /149/ and Brewer /150/ give the more reliable value $\Delta H^0_{298} = -489.0$ kcal/mole,

If we use this value and the equations for the heat capacities of Ta, Ta_2O_5, and O_2 recommended above, we obtain the following expression for the heat of formation of Ta_2O_5 (from 298 to 1800°K):

$$\Delta H_T^\circ = -491{,}550 + 4.58 \cdot T + 8.70 \cdot 10^{-3} T^2 + 1.22 \cdot 10^5 T^{-1}.$$

From this equation the following values are obtained:

t, °C	25	500	1500
$-\Delta H_T^0$, cal/mole	489,000	482,650	456,010

Entropy of formation of Ta_2O_5. The entropy of formation of tantalum pentoxide according to the reaction $2Ta + \frac{5}{2}O_2 = Ta_2O_5$ may be calculated from the above values of S_{298}^0 as $\Delta S_{298}^0 = -108.19$ cal/mole · degree.

Free energy of formation of Ta_2O_5. From the above values and the third law of thermodynamics, we obtain $\Delta F_{298}^0 = -456.74$ kcal/mole. Using $\Delta H_{298}^0 = -489.0$ kcal/mole and the heat capacities of Ta (p. 191), Ta_2O_5 (p. 199), and O_2 (p. 169), we may derive the following equation:

$$\Delta F_T^\circ = -491{,}550 - 10.548\, T \log T - 8.70^{-3} T^2 + 0.61 \cdot 10^5 T^{-1} + 144.7\, T. \quad (1)$$

Kubaschewski and Evans /31/ propose the following equation for the free energy of formation of Ta_2O_5:

$$\Delta F_T^\circ = -491{,}550 - 20.7\, T \log T + 168.4\, T. \quad (2)$$

The following values are obtained from the above equations:

t, °C	25	500	1000	1500
$-\Delta F_T^0$, cal/mole /1/	456,740	404,370	363,090	323,070
$-\Delta F_T^0$, cal/mole /2/	456,580	407,540	358,940	312,160

38. HALIDES OF TANTALUM

Tantalum pentachloride $TaCl_5$ (M = 358.235)

Tantalum pentachloride crystallizes in the monoclinic system (isomorphic with $NbCl_5$) and has the following lattice parameters: a_0 = 18.23 Å; b_0 = 17.76 Å; c_0 = 5.86 Å; β = 90.6° /154/.

Density of $TaCl_5$. The density of $TaCl_5$ is 3.68 g/cm³ /154–156/.

Melting point of $TaCl_5$. According to various authors the melting point of tantalum pentachloride lies between 204 and 221°. The most recent values are 216.5° /28/ and 215° /27/.

Vapor pressure of $TaCl_5$. The normal boiling point of $TaCl_5$ is between 233 and 242° /23, 25–27, 30, 158/. The boiling points at various pressures were determined by Tarasenkov and Komandin /25/ and Ainscough, Holt, and Trowse /27/. The dynamic method was used by Opykhtina and Fleisher /30/, while Tarasenkov and Komandin /25/ and Alexander and Fairbrother /26/ used the static method. The results of these authors are shown in Table 238.

TABLE 238

Vapor pressure of $TaCl_5$

t, °C	P, mm Hg	Reference	t, °C	P, mm Hg	Reference	t, °C	P, mm Hg	Reference
28	1	/25/	181.5	67.3	/26/	223.4	498.4	/26/
36	2	/25/	184	87	/25/	225	605.3	/30/
50	2.5	/25/	188.6	97.6	/26/	227	594	/25/
70	3.0	/25/	195	144	/25/	227.4	558.5	/26/
100	4.0	/25/	196.0	141.1	/26/	230	698.0	/30/
120	5.0	/25/	197	176	/25/	230.1	595.7	/26/
120	2.1	/30/	199.5	205	/25/	231	668.	/25/
139.1	4.8	/26/	200.7	180.2	/26/	232	684	/25/
141	13.0	/25/	203	241	/25/	233	760.0	/30/
143	9.0	/30/	205	325.6	/30/	233.5	696	/25/
143	9.9	/30/	205.9	228.8	/26/	234	724	/25/
150.8	11.3	/26/	210	387.2	/30/	234.3	671.5	/26/
159	23.7	/30/	210.7	291.2	/26/	235.5	732	/25/
161	20.4	/26/	214.8	348.4	/26/	236.5	761	/25/
162	33.0	/25/	218.7	418.6	/26/	237.5	780	/25/
169	46	/25/	219	534.9	/30/	238	790	/25/
170	52.9	/30/	221	565.2	/30/	238. 1	741.7	/26/
173.6	42.9	/26/	221	535	/25/	238.5	798	/25/
174	58	/25/	221.1	468.5	/26/			
178	70	/25/	222	538	/25/			
180	89.4	/30/						

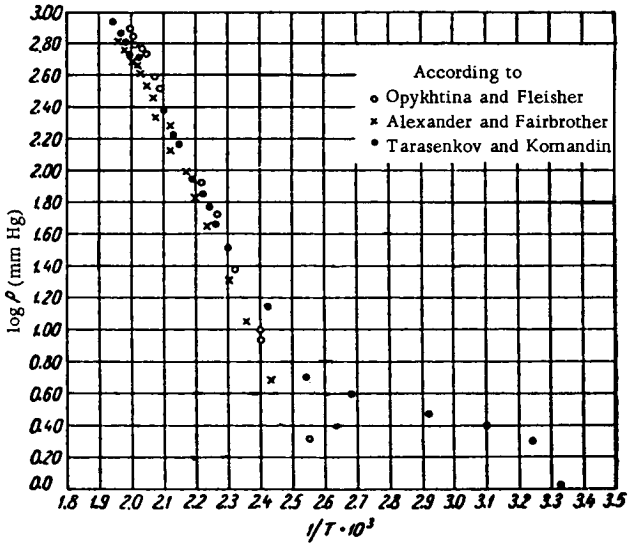

Figure 7. Vapor pressure of $TaCl_5$

Ainscough, Holt, and Trowse /27/ give their results only in the form of graphs and propose the following equation for the vapor pressure of $TaCl_5$ from 680 to 900 mm Hg (cf. also Figure 7):

$$\log P(\text{mm Hg}) = 8.543 - \frac{2865}{T}.$$

From the above equation the following values are obtained:

t, °C	220	230	240	250
P, mm Hg	540	703	908	1161

Heats of fusion, sublimation, and vaporization of $TaCl_5$. Rossini /29/ gives the heat of fusion of tantalum pentachloride as 11.1 kcal/mole at 484°K; Kubaschewski and Evans /31/ quote 8.2 kcal/mole at 22°. Opykhtina and Fleisher /30/ calculated the heat of sublimation of $TaCl_5$ from their vapor pressure data as 21.6 kcal/mole between 122 and 233°. Rossini /29/ gives $L_{subl} = 25.2$ kcal/mole at 484°K, whereas Kubaschewski and Evans /31/ consider the most reliable value for the heat of sublimation to be 21.28 kcal/mole (240°). Ainscough, Holt, and Trowse /27/ measured the vapor pressure of $TaCl_5$ and calculated its heat of vaporization as 13.1 kcal/mole.

Heat of formation of $TaCl_5$. Schafer and Kahlenberg /33/ and Shchukarev /159/ measured the heat of formation of tantalum pentachloride according to the reaction $Ta(s) + 2.5Cl_2(g) \rightarrow TaCl_5(s)$. Using the heat of solution method, they obtained the following results: $\Delta H^0_{298} = -205.0$ kcal /33/ and $\Delta H^0_{298} = -206.0$ kcal/159/. The data of other authors /160–163/, frequently based only on estimation, vary from $-\Delta H = 133$ to 360 kcal/mole and are therefore less reliable.

Tantalum pentabromide $TaBr_5$ ($M = 580.53$)

Tantalum pentabromide crystallizes in the orthorhombic system and is isomorphic with $NbBr_5$. The lattice parameters of $TaBr_5$ are $a_0 = 6.125$ Å, $b_0 = 12.92$ Å, and $c_0 = 18.60$ Å /154/.

Density of $TaBr_5$. The density of $TaBr_5$ determined by the pycnometric method is $d = 4.99$ g/cm^3 /154/. The X-ray density of $TaBr_5$ is $d = 5.238$ g/cm^3 /154/. The melting point of this compound is 280.0° or 267°, according to /26/ and /164/, respectively.

Vapor pressure of $TaBr_5$. The normal boiling point of this compound is 348.8° or 345°, according to /26/ and /164/, respectively. Table 239 presents the data of Alexander and Fairbrother /26/ and of Wiseman and Gregory /164/ on the vapor pressure of this compound. These data were obtained by the static method.

The data of Wiseman and Gregory /164/ were found to conform to the following equations:

for liquid $TaBr_5$ from 267 to 345°:

$$\log P(\text{mm Hg}) = 8.171 - \frac{3265}{T};$$

and for solid $TaBr_5$ from 200 to 267°:

$$\log P(\text{mm Hg}) = 12.571 - \frac{5650}{T}.$$

Heats of fusion, vaporization, and sublimation of $TaBr_5$. Rossini /29/ and Kubaschewski and Evans /31/ give the heat of fusion of $TaBr_5$ as 10.7 kcal/mole and 10.9 kcal/mole, respectively.

TABLE 239

Vapor pressure of $TaBr_5$

t, °C	P, mm Hg	Reference	t, °C	P, mm Hg	Reference	t, °C	P, mm Hg	Reference
211	4.1	/26/	244	43	/164/	299.3	267.6	/26/
213	10	/164/	246	47	/164/	302	321	/164/
213	9	/164/	256	80	/164/	304	330	/164/
215	11	/164/	256	78	/164/	305.5	311.0	/26/
217	11	/164/	256.2	62.5	/26/	310	343	/164/
218	11	/164/	257	83	/164/	311.6	354.7	/26/
223	15	/164/	261	105	/164/	320.0	421.2	/26/
224	17	/164/	266	122	/164/	322.4	443.5	/26/
225.5	12.9	/26/	269.1	112.9	/26/	324	500	/164/
226	18	/164/	270	135	/164/	324	466	/164/
226	16	/164/	270	145	/164/	328.7	507.8	/26/
231	24	/164/	274	163	/164/	329	546	/164/
232	24	/164/	282.0	176.8	/26/	333.4	560	/26/
234	26	/164/	285	213	/164/	338.7	624.4	/26/
235	27	/164/	290	215	/164/	342	708	/164/
238	35	/164/	292.2	228.3	/26/	343.4	683.9	/26/
240	35	/164/	295	277	/164/	348.8	756.9	/26/
240.3	28.5	/26/	297	256	/164/			

The heat of vaporization of $TaBr_5$ is 14.9 kcal/mole between 290 and 350° /26/ or between 267 and 345° /164/. Rossini /29/ gives 14.6 kcal/mole as the heat of vaporization of tantalum pentabromide at its boiling point, Kubaschewski and Evans /31/ give 14.9 kcal/mole.

The heat of sublimation of this compound is 25.8 kcal/mole between 250 and 280° /26/ or from 200 to 267° /164/.

Heat of formation of $TaBr_5$. The heat of formation of $TaBr_5$ according to the reaction $Ta\,(s) + \frac{5}{2}Br_2\,(g) \rightarrow TaBr_5\,(s)$ was determined from the heat of solution of tantalum pentabromide and is given by $\Delta H^0_{298} = -164.0$ kcal /159/. For the heat of formation of $TaBr_5$ Brewer /162/ gives the estimated value $\Delta H^0_{298} = -128$ kcal/mole, which is however less reliable.

Tantalum pentafluoride TaF_5 (M = 275.88)

There are no available data on the structure of TaF_5.

Density of TaF_5. The density of solid TiF_5 is 4.981 g/cm^3 at 15°, and 4.44 g/cm^3 at 19.5° /39/.

Melting point of TaF_5. Ruff and Schiller /39/ determined the melting point of this compound as 96.8°. Fairbrother and Frith /40/ give 95.1°.

Vapor pressure of TaF_5. The normal boiling point of TaF_5 is 229.2° /39, 40/. Table 240 presents the vapor pressure of TaF_5 obtained by means of the static method /39, 40/.

TABLE 240

Vapor pressure of TaF_5

t, °C	P, mm Hg	Reference	t°, C	P, mm Hg	Reference	t°, C	P, mm Hg	Reference
84.5	2.7	/40/	175.9	165.0	/40/	204	485.8	/39/
89.6	3.6	/40/	182.1	191.4	/40/	206.4	410.4	/40/
99.7	7.8	/40/	183.	368.2	/39/	208.5	417.3	/40/
109.1	14.6	/40/	183.3	214.4	/40/	212.2	491.0	/40/
120.9	20.7	/40/	187.3	237.7	/40/	212.5	540.8	/39/
136.5	38.0	/40/	192.1	282.7	/40/	223.4	642.0	/40/
147.5	61.3	/40/	196.4	307.3	/40/	227.5	720.7	/39/
152.3	67.2	/40/	198.5	477.3	/39/	228.2	733.7	/40/
160.7	99.5	/40/	199.1	337.7	/40/	228.8	741.9	/40/
162.2	105.3	/40/	200.9	334.6	/40/	228.9	753.7	/39/
172.5	143.4	/40/	203.9	393.1	/40/			

The experimental data of Fairbrother and Frith /40/ were found to conform to the following equation from 80.0 to 228.8°:

$$\log P(\text{mm Hg}) = 8.254 - \frac{2834}{T},$$

from which the heat of evaporation of tantalum pentafluoride is 13.0 kcal/mole.

Tantalum pentaiodide TaI_5 (M = 815.5)

Tantalum pentaiodide crystallizes in the orthorhombic system and has the following lattice parameters: a_0 = 6.65 Å, b_0 = 13.95 Å, and c = 20.10 Å /154/.

Density of TaI_5. According to /154/, the density of this compound is 5.80 g/cm³.

Melting point of TaI_5. Tantalum pentaiodide melts at 496° /26/.

Vapor pressure of TaI_5. Alexander and Fairbrother /26/ measured the vapor pressure of TaI_5 using a static method. Their experimental data are given in Table 241. The boiling point of this compound is 543° at normal pressure.

TABLE 241

Vapor pressure of TaI_5

t°, °C	P, mm Hg	t°, °C	P, mm Hg	t°, °C	P, mm Hg	t°, °C	P, mm Hg
307.7	5.8	391.7	54.5	455.8	192.3	500.4	421.2
320.0	7.6	402.5	67.2	464.3	226.2	509.0	469.4
334.3	9.9	411.1	81.4	466.8	236.6	518.5	547.3
350.3	16.0	419.5	95.6	478.5	288.7	524.5	590.4
363.7	25.7	428.7	117.5	485.4	322.4	531.0	650.4
372.7	35.1	437.9	138.1	492.1	362.1	539.1	727.4
382.8	44.0	449.4	172.6	493.0	373.1		

Alexander and Fairbrother /26/ calculated the heats of vaporization, sublimation, and fusion from their vapor pressure data and obtained the following values: L_{vap} = 18.1 kcal/mole, L_{subl} = 19.7 kcal/mole and L_{fus} = 1.6 kcal/mole.

Lower halides of tantalum

The lower halides of tantalum have been considerably less studied. Roth and Becker /96/ give the estimated value $\Delta H^0_{298} = -346$ kcal/mole for $TaCl_3$.

39. CARBIDES OF TANTALUM

Various authors have verified the existence of the following carbides in the Ta—C system: Ta_2C /64, 165—167/ and TaC /44, 45, 47, 49, 64, 166—169/. The carbide Ta_2C has a rather limited homogeneity field /166/. $TaC_{0.38-0.50}$ /165/ has a hexagonal close-packed structure. The parameters of the lattice of Ta_2C are as follows: a = 3.091 Å, c = 4.93 Å, and c/a = 1.595 /64/. According to /167/, Ta_2C may, like W_2C, occur in two allotropic modifications. The parameter of the crystalline lattice of TaC (face-centered NaCl type) is a_0 = 4.455 Å /64/. According to /165/ the higher carbide of tantalum has a homogeneity field expressed by the formula $TaC_{0.58-0.91}$.

Density of TaC. The density of tantalum monocarbide is 13.96 g/cm³ /54/, 14.05 g/cm³ /170/, or 14.48 g/cm³ /45/. The X-ray density is 14.53 g/cm³ /64/.

Melting point. Tantalum monocarbide melts between 4000 and 4100°K /54/. Other authors report that the melting point of TaC is 3880 ± 150° /46/ or 3800° /166/. Ta_2C melts at 3400° with simultaneous decomposition /166/.

Heat capacity of TaC. The heat capacity of the carbide TaC was determined by Kelley /148/ at low temperatures. His data are given in Table 242.

TABLE 242

Heat capacity of TaC

T, °K	C_p cal/mole·deg	T, °K	C_p cal/mole·deg	T, °K	C_p cal/mole·deg	T, °K	C_p cal/mole·deg
54.6	2.275	84.9	3.924	164.6	6.141	244.7	7.912
58.1	2.505	94.5	4.271	174.2	6.377	253.1	8.109
62.1	2.759	104.3	4.583	184.5	6.614	265.3	8.280
66.5	3.032	114.7	4.876	194.3	6.843	275.1	8.424
71.7	3.298	124.8	5.149	204.5	7.078	284.6	8.559
75.6	3.525	134.8	5.415	214.6	7.292	293.9	8.741
80.2	3.735	144.8	5.661	224.5	7.514	294.5	8.764
80.6	3.752	154.5	5 900	234.5	7.713	298.16	(8.79)
84.4	3.903						

Kubaschewski and Evans /31/ give the following equation for the heat capacity of TaC:

$$C_p = 7.28 + 1.65 \cdot 10^{-3} T \text{ (for 298 to 2000°)}$$

The following values are obtained from the above equation:

t, °C	25	500	1000	1500
C_p, cal/mole·deg	7.77	8.56	9.38	10.21

Entropy of TaC. From his data on the heat capacity of TaC at low temperatures, Kelley /148/ determined its entropy as $S^0_{298} = 10.11 \pm 0.08$ cal/mole · degree.

Heat of formation of tantalum carbides. Humphrey /153/ determined the heat of formation for the reaction $TaC + \frac{9}{4} O_2 = \frac{1}{2} Ta_2O_5 + CO_2$ by combustion in a calorimetric bomb and obtained the result: $\Delta H^0_{298} = -300.0$ kcal. The author used the heats of formation of tantalum pentoxide, $\Delta H^0_{298} = -488.8$ kcal/mole /153/, and of carbon dioxide, $\Delta H^0_{298} = -94.05$ kcal/mole /29/, to calculate the heat of formation of TaC as $\Delta H^0_{298} = -38.5$ kcal/mole.

Smirnova and Ormont, using the same method /165/, calculated the heats of formation of carbides of various compositions. Their results are presented in Table 243. The authors used the following data for their calculations: the heat of formation of tantalum pentoxide is $\Delta H^0_{298} = -480.0$ kcal/mole /165/, and that of carbon dioxide is $\Delta H^0_{298} = -94.05$ kcal/mole /29/.

Free energy of formation of tantalum carbides. Humphrey used the standard entropy of TaC (10.1 e. u.) /148/ to calculate the free energy of formation as $\Delta F^0_{298} = -38.1$ kcal/mole /153/.

Table 243 contains the free energies of formation of tantalum carbides of various composition, as calculated by Smirnova and Ormont /165/. The

TABLE 243

Heat and free energy of formation of tantalum carbides

Stoichiometric and phase composition	$-\Delta H^0_{298}$, kcal	$-\Delta F^0_{298}$, kc l
(TaC)	(36.0)	(35.7)
$TaC_{0.90}$	31.7	31.5
$TaC_{0.80}$	25.5	25.4
$TaC_{0.70}$	21.5	21.4
$TaC_{0.60}$	18.7	18.6
$TaC_{0.50}$	17.0	16.8
$TaC_{0.40}$	15.5	15.3

NOTE. The carbides TaC_x ($0.38 < x < 0.50$) occur in the hexagonal β- phase region, whereas the carbides TaC_x ($0.58 < x < 0.91$) are in the cubic γ-phase region.

standard entropies of the carbides TaC_x were calculated by these authors from the standard entropies of tantalum and graphite.

40. NITRIDES OF TANTALUM

According to various authors the following nitrides exist in the tantalum-nitrogen system: TaN /47, 64, 168, 171—173/ and Ta_2N /173—174/. Tantalum nitride crystallizes in the hexagonal system with the lattice parameters a = 3.05 Å and c = 4.95 Å /164/.

TABLE 244

Values for the heat capacity of TaN, calculated from equations (1), (2), and (3)

Temperature, °C	C_p, cal/mole·deg		
	(1)	(2)	(3)
25	10.05	9.65	9.70
500	13.76	14.33	13.56

Density of TaN. The density of TaN is 14.1 g/cm³ /60/.

Heat capacity of TaN. Kubaschewski and Evans /31/ give the following equation for the heat capacity of TaN from 298 to 800°K:

$$C_p = 7.73 + 7.80 \cdot 10^{-3} T. \quad (1)$$

Smithells /175/ gives the following equation, valid from 273 to 774°K:

$$C_p = 4.74 + 19.87 \cdot 10^{-3} T - 11.32 \cdot 10^{-6} T^2. \quad (2)$$

Britske et al. /94/ propose the following equation for the temperature range 273 to 773°K:

$$C_p = 10.23 + 4.70 \cdot 10^{-3} T - 1.81 \cdot 10^{5} T^{-2}. \quad (3)$$

The values for C_p determined from these equations are given in Table 244. Equations (1) to (3) were apparently derived from the data of Satoh /178/ on the mean heat capacities of TaN:

$\overline{C}_p$ = 9.98 (for 273 to 373°K);

$\overline{C}_p$ = 11.0 (for 273 to 573°K);

$\overline{C}_p$ = 11.84 (for 273 to 773°K).

Dissociation pressure of the tantalum nitrides. Slade and Higson /176/ determined the dissociation pressure of tantalum nitride at two temperatures: $P_{N_2} = 5.92 \cdot 10^{-4}$ atm. at 1443° and $P_{N_2} = 1.32 \cdot 10^{-3}$ atm. at 1581°.

Heat of formation of the tantalum nitrides. Neumann, Kröger, and Kunz /177/ carried out the combustion of TaN in a calorimetric bomb. For combustion according to the reaction

$$TaN + \frac{5}{4}O_2 = \frac{1}{2}Ta_2O_5 + \frac{1}{2}N_2,$$

they obtained $\Delta H^0_{298} = -191.4$ kcal. Mah and Gellert /179/ obtained for the same reaction $\Delta H^0_{298} = -184.4$ kcal. Neumann et al. /177/ calculated the heat of formation of TaN as $\Delta H^0_{298} = -58.1$ kcal/mole, Mah and Gellert

/179/ as $\Delta H^0_{298} = -60.0$ kcal/mole. Rossini et al. /29/ give $\Delta H^0_{298} = -58.2$ kcal/mole.

Mah /180/ ignited Ta_2N in a calorimetric bomb and obtained $\Delta H^0_{298} = -424.1$ kcal for the heat of the reaction

$$Ta_2N + \frac{5}{2}O_2 = Ta_2O_5 + \frac{1}{2}N_2.$$

From this value the heat of formation of Ta_2N was calculated: $\Delta H^0_{298} = -64.7$ kcal/mole.

Free energy of formation of TaN. Kubaschewski and Evans /31/ give the following approximate equation for the free energy of TaN:

$$\Delta F^\circ_T \text{ (cal/mole)} = -58{,}900 - 6.9\,T \log T + 39.85\,T,$$

from which $\Delta F^0_{298} = -52.1$ kcal/mole.

41. SILICIDES OF TANTALUM

Various authors found the following silicides in the tantalum-silicon system: $TaSi_2$ /181—184/; Ta_5Si_3 ($TaSi_{0.6}$) /183—187/; Ta_2Si ($TaSi_{0.4}$) /183—184/; and $Ta—Si_{0.20-0.22}$ /183—184/. Two different modifications of $TaSi_{0.22}$ are discussed by /183 and 184/. Three different modifications of $TaSi_{0.6}$ exist according to /183—187/. For the silicide $TaSi_2$, various authors /182—184/ give the same hexagonal structure with the following lattice parameters: $a = 4.773$ Å, $c = 6.552$ Å /182/.

Melting point. The silicide $TaSi_2$ melts at 2400° /64/. The eutectic melting points in the Ta—Si system /183/ are given below:

$TaSi_2 — TaSi_{0.6}$	1770
$TaSi_{0.6} — TaSi_{0.4}$	1610
$TaSi_{0.4} — TaSi_{0.2}$	1910
$TaSi_{0.2}$ — Ta	2110

TABLE 245

Free energy of formation of the tantalum silicides

T, °K	$P_{(1)}$, 10^7	$\Delta F^0_{(1)}$, kcal	T, °K	$P_{(2)}$, 10^7	$\Delta F^0_{(2)}$, kcal	T, °K	$P_{(3)}$, 10^7	$\Delta F^0_{(3)}$, kcal	T, K°	$P_{(4)}$, 10^6	$\Delta F^0_{(4)}$, kcal
2233	2.62	67.26	2216	7.57	62.07	2033	4.70	58.88	1903	1.21	61.55
2235	5.38	64.12	2241	11.2	61.02	2105	12.3	56.92	1912	1.80	50.25
2259	2.90	67.59	2262	17.5	59.56	2147	17.9	56.47	2004	4.73	48.82
2283	4.78	66.02	2300	27.5	58.54	2161	17.3	56.96	2011	5.08	48.69
2329	10.05	63.72	2316	42.8	56.90	2213	47.8	53.89	2013	4.55	49.20
2329	11.1	63.47	2324	37.1	57.75	2238	55.0	53.87	2037	8.19	47.42
2309	7.14	65.00	2346	50.9	56.82	2271	71.1	53.37	2050	8.92	47.38
2391	34.7	59.73	2373	52.1	57.38	2304	138	51.36	2054	9.29	47.28
2401	37.5	59.62	2387	92.1	55.00	2313	189	50.01	2118	23.1	44.92
2432	39.4	60.14	2419	112	54.81				2141	30.4	44.25
2441	46.1	59.61	2420	97.9	55.47				2164	68.4	41.25
2445	47.7	59.54									
2488	78.4	58.14									

Dissociation pressure of the tantalum silicides. Using the Knudsen cell method, Meyer and Searcy /188/ determined dissociation pressures of the silicides: $TaSi_{0.22}$, Ta_2Si, $TaSi_{0.60}$, and $TaSi_2$ according to the following reactions:

$$4.5TaSi_{0.22} = 4.5Ta + Si(g); \quad (1)$$

$$^9/_5Ta_2Si = ^{18}/_5TaSi_{0.22} + Si(g); \quad (2)$$

$$10TaSi_{0.6} = 5Ta_2Si + Si(g); \quad (3)$$

$$^5/_7TaSi_2 = ^5/_7 Ta_2Si_{0.6} + Si(g). \quad (4)$$

Table 245 shows the experimental values for P_{Si} in atmospheres, according to /188/ and calculated values of ΔF_T° for reactions (1) to (4).

Heat of formation of the silicides of tantalum. From their data on the dissociation pressures of tantalum silicides, Meyer and Searcy /188/ calculated the following changes in the heat contents of reactions (1) to (4) at 298°K: $\Delta H^0_{(1)}$ = 146.4 kcal; $\Delta H^0_{(2)}$ = 137.2 kcal; $\Delta H^0_{(3)}$ = 125.6 kcal; $\Delta H^0_{(4)}$ = 117.2 kcal. Hence the standard heats of formation of the respective compounds formed from tantalum and solid silicon are as follows:

$4.5TaSi_{0.22}$. $\Delta H^\circ_{298} = -34.4$ kcal;

$1Ta_2Si$. $\Delta H^\circ_{298} = -29.3$ kcal;

$1.67TaSi_{0.6}$. $\Delta H^\circ_{298} = -26.7$ kcal;

$^1/_2TaSi_2$. $\Delta H^\circ_{298} = -11.6$ kcal.

These data show good agreement with those of Robins and Jenkins /189/, obtained by calorimetric measurements:

$1.67TaSi_{0.6}$. $\Delta H^\circ_{298} = -25.3$ kcal;

$^1/_2TaSi_2$. $\Delta H^\circ_{298} = -13.9$ kcal.

42. HYDRIDES OF TANTALUM

The absorption of hydrogen by metallic tantalum at different pressures and temperatures was studied by various authors /5, 200, 201, 202, 203, 214/. Sieverts and co-workers /202, 203/ found that the absorption of hydrogen by tantalum decreases with temperature according to the square root law. Table 246 shows the values of these authors for the solubility of hydrogen in metallic tantalum at 760 mm Hg.

Recent data of Perminov /194/ on the solubility of hydrogen in tantalum between 620 and 680° show very good agreement with the results obtained by Sieverts /203/.

The absorption isotherms of hydrogen by tantalum at 164 to 402°, studied by Kufstad, Wallace, and Hydönen /204/, indicate the formation of solid interstitial solutions from 0 to 33.5 at. % hydrogen, i. e., up to $TaH_{0.503}$, and the validity of the square root law for concentrations of hydrogen from 2 to 33.5 at. %.

Sieverts and Gotta /152/ report that the maximum content of hydrogen in tantalum hydride corresponds to the formula $TaH_{0.78}$ (or 795 volumes of H_2 per unit volume of Ta).

TABLE 246

Solubility of hydrogen in metallic tantalum

t, °C	Solubility, mg H_2/100 g Ta	t, °C	Solubility, mg H_2/100 g Ta	t, °C	Solubility, mg H_2/100 g Ta
17	417	474	157	830	20.2
100	409	530	107	930	14.9
183	377	630	51.2	1030	11.4
263	327	730	33.4	1230	8.17
314	297	780	29.7	1330	6.66
417	212				

Gulbransen and Andrew /205, 206/ showed that the formation of tantalum hydride starts at 340°. The absorption of hydrogen by tantalum increases up to 460° followed by a subsequent decrease. At temperatures above 539°, the absorption again increases. This phenomenon is caused by formation of hydrides of varying degrees of thermal stabilities. The low-temperature hydride exists at temperatures below 350° in vacuo (10^{-6} mm Hg), whereas the high-temperature hydride is stable in high vacuo at temperatures between 700 and 900°. The phase composition of hydrogen tantalum solutions at different temperatures was studied by various authors using X-ray methods. Thus, Hagg /207/ found that at 600° the following phases occur in the Ta—H system:

1. α-phase corresponding to a solid interstitial solution of hydrogen in a body-centered cubic lattice of tantalum (from 0 to 12 at. % H, i. e., $TaH_{0.14}$).

2. β-phase, Ta_2H, (or 33 at. % H), having a densely packed hexagonal lattice consisting of Ta atoms. The homogeneity range is very small: $a = 3.094$ κX; $c = 4.923$ κX.

3. γ-phase corresponding to TaH (46 to 47 at. % H) with a face-centered orthorhombic structure and the following lattice parameters: $a = 4.811$ κX; $b = 4.781$ κX, and $c = 3.434$ κX. Stalinsky /20/ also reports the existence of a two-phase region between the Ta phase and an orthorhombic region of the composition $TaH_{0.37}$ to $TaH_{0.47}$ (27 to 32 at. % H) at 300°.

The solubility of hydrogen in tantalum is 16.7 at. % H at 400 to 500° /203/ and 34 at. % H at 20°, i. e., $TaH_{0.2}$ /209/. Brauer and Hermann /210/, however, found the solubility of hydrogen in tantalum at 20° to be 17 at. % H.

Waite, Wallace, and Craig /211/ studied the solubility of hydrogen in tantalum; on decreasing the temperature from +50 to −145°, it changes from ~ 40 to 0 at. % H and a hydride phase of the approximate composition Ta_2H with a tetragonal lattice, $a = 3.38$ Å and $c = 3.41$ Å, crystallizes out from the solid solution.

Krylov and Anan'in /212/ obtained hydrides with higher hydrogen contents corresponding to the formulas TaH, TaH_2, and TaH_3 from reaction of $TaCl_5$ with Grignard reagents (in an atmosphere of H_2 and N_2).

The hydride TaH is stable at room temperature and normal atmospheric conditions. It starts to decompose at temperatures above 100°. The ignition temperature of TaH is 300° /213/. The density of $TaH_{0.76}$ is 15.1 g/cm^3 /152/.

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